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PART II.

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General and Physical Chemistry.

A New Method of Expressing the Formulæ of Line Spectra ALFRED LARTIGUE (*Compt. rend.*, 1919, **169**, 914—915).—In place of the general formula $10^8/\lambda = N_0(1/p^2 - 1/q^2)$ waves per cm., the author proposes to use the formula $\lambda_m = (4 \times 10^8/N_0)(p/2)^3[2/p + 1/m - 1/(m+2p)]$ Ångströms, where $m = q - p$. W. G.

Luminous Phenomena Observed in the Neighbourhood of a Plate of Graphite raised to a High Temperature by means of an Electric Current. G. A. HEMSALECH (*Compt. rend.*, 1919, **169**, 915—918).—A sheet of graphite 0·95 mm. thick had its upper surface covered with a thin layer of carborundum powder, and an electric current was passed through it. As the temperature of the plate increased, when it became incandescent, yellow vapours appeared above the plate and were carried upwards by the air convection currents. When the temperature of the plate reached 2500—2700°, the space bounded by the plate and the air convection currents became filled with a luminous vapour which gave a spectrum composed of rays and bands, whilst the yellow vapours became blue and also luminous, and gave a continuous spectrum. When the temperature of the plate reached 3000°, a red fringe appeared on its lower surface and in contact with it, and was formed by the passage of an electric current through the conducting vapours. Its position could be controlled

by means of the magnetic field from a powerful electro-magnet. This red fringe is of electrical origin, and is probably due to a current of electrons, which decompose the molecules and create centres of emission differing from those of the luminous vapour.
W. G.

The Spectra Emitted by the Red Fringe and the Luminous Vapour in the Neighbourhood of an Incandescent Plate of Graphite. G. A. HEMSALECH (*Compt. rend.*, 1919, **169**, 1034—1036).—It has previously been shown that the luminous vapour and red fringe obtained when a plate of graphite is raised by an electric current to high temperatures emit discontinuous spectra (preceding abstract). These spectra have now been examined in detail, and the rays which have been detected are given and the influence of a magnetic field on the centres of emission examined. The spectra of bands and rays, obtained under the experimental conditions, owe their origin to two different types of centres of emission: (1) Those created by the action of heat on the carbides of the metals, the spectrum of which is regulated by the temperature of the graphite plate. The centres of emission are not sensibly influenced by a magnetic field. (2) Those produced by the thermo-electric current, the spectrum of which is regulated both thermally and electrically. The centres of emission are, in this case, very sensitive to magnetic forces. W. G.

Reduction Spectra, and in particular that of Magnesium and its Compounds. J. MEUNIER (*Bull. Soc. Chim.*, 1919, [iv], **25**, 562—565).—Using the method previously described, by reduction in a hydrogen flame (compare A., 1919, ii, 132) the author finds in the ultraviolet region the band composed of the rays $\lambda = 3810$, 3829, 3833, 3838, 3851, 3858, 3861, and another band consisting of the rays $\lambda = 3885$, 3912, 3940, 3960, 3980. Nine other rays between $\lambda = 3700$ and 3780 have been noticed and their wavelengths approximately determined. Of the salts of magnesium, the chloride, oxychloride, sulphate, nitrate, oxide, and carbonate gave the above spectrum. The pyrophosphate is not, apparently, reduced under these conditions and does not give the above spectrum, phenomena of incandescence, corresponding with the continuous spectrum, being produced.

In some cases, the γ-ray in the neighbourhood of $\lambda = 5003$, and the broad magnesium ray, $\lambda = 4702$, are obtained. W. G.

The *X*-ray Spectrum of Tungsten. M. DE BROGLIE (*Compt. rend.*, 1919, **169**, 962—965).—Certain observations, as a result of a long series of experiments, are made on the results of Overn and of Siegbahn (A., 1919, ii, 488) on the spectrum of tungsten. Some of the lines mentioned by Overn the author has not found, whilst on the other hand he has observed certain rays not mentioned by Overn.

For the purpose of obtaining weak bands the ...

the use of a metal shutter pierced with a slit and travelling in front of the sensitive plate with a velocity such that, during the rotation of the crystal, the reflected ray passes continuously through the slit. W. G.

Relative Brightness of Dark Radiation at the Melting Points of Gold and Palladium. FR. HOFFMANN and W. MEISSNER (*Ann. Physik*, 1919, [iv], **60**, 201—232).—The relative brightness of the dark radiation at the melting points of gold and palladium has been measured by two different methods: first, by use of an improved hollow radiator constructed on the Lummer-Kurlbaum principle, whereby the melting point was determined inside the radiator by the wire method; secondly, by use of a hollow radiator which was immersed in the molten metal. The measurements of brightness were made with a König-Martens spectrophotometer. The relative brightness at the melting points of gold and palladium is expressed by 81·5 at the wave-length of $0·6563\mu$. The palladium used had the same melting point as that used by Day and Sosman in the gas thermometric measurements. Palladium prepared by repeated precipitation of the ammonium double chloride by means of mercury cyanide gave a very constant melting point, and would serve excellently as a fixed point for temperature determinations. Using $c=14,300$ as the radiation constant and 1063° as the melting point of gold, it is found that 1557° is the melting point of palladium. This value is about 8° higher than Day and Sosman's figure, 1549·2°. J. F. S.

The Ozonogenic Power of the Solar Radiation at the Altitude of the Observatory of Mont Blanc. RAOUL BAYEUX (*Compt. rend.*, 1919, **169**, 957—959).—At an altitude of 4360 metres, the solar radiation does not cause the polymerisation of oxygen to ozone. W. G.

The Absorption of Light by Gases. G. RIBAUD (*Ann. Physique*, 1919, [ix], **12**, 107—226).—A study of the continuous absorption by bromine vapour in the ultraviolet portion of the spectrum, the conditions being varied as much as possible, the temperature range rising to 620°. The observed experimental curves show notable systematic divergences from the theoretical curves based on the electromagnetic theory of absorption, the weakening (amortissement), in particular, calculated for the different regions of the curve, not having the same value. The kinetic theory does not apply to the broad, continuous regions of absorption, and the mechanism of the absorption must be sought in the molecule itself. The author is of the opinion that the weakening (amortissement) can be explained by the disturbances of the electron in the interior of the molecule. This conception permits of an explanation of the fact that the breadth of the bands goes on increasing from the ultraviolet to the infra-red.

It is shown that Königsberger's law, that the breadth of the

band is proportional to the square root of the temperature, must be rejected.

In the last part of the paper it is shown that the absorption by the rays of bromine vapour is in close accord with a kinetic theory of absorption, and, in this case, the mobile corpuscle containing the electron is, in all probability, the molecule itself. The magneto-optical properties of the vapours of bromine and iodine in the neighbourhood of the absorption rays have been studied, and it is shown that the rotatory phenomenon observed in the neighbourhood of these rays in iodine vapour is due to a very weak Zeeman effect. The smallness of this effect agrees moderately well with the small values observed for the ratio e/m in the absorption study. W. G.

Chemical Actions of Light. E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 432—436).—When subjected to prolonged exposure to light, ethyl alcohol does not undergo oxidation, but in presence of oxalic acid it is slowly oxidised in the light, yielding carbon dioxide and formic and acetic acids. Under similar conditions, glycerol (8 grams) gives carbon dioxide, together with other oxidation products equivalent, in their reducing action on Fehling's solution, to 0·351 gram of dextrose. When exposed to light in an atmosphere of oxygen and in presence of water, thiophen yields carbon dioxide and formic, oxalic, and sulphuric acids. Similarly, a benzene solution containing benzophenone and dibenzyl gives rise to benzophenonepinacone and *triphenylbenzylethanol* [*ααβγ-tetraphenylpropyl alcohol*], $OH\cdot CPh_2\cdot CHPh\cdot CH_2Ph$, which crystallises in long needles, m. p. 165°. In the light, benzoquinone and toluene react to form quinol, quinhydrone, and a small proportion of benzaldehyde. Acetone and *iso*amyl alcohol also react under these conditions, the products identified being (1) *iso*propyl alcohol; (2) *dimethyl*iso*butylethylene glycol* [*βε-dimethylhexane-βγ-diol*], $CHMe_2\cdot CH_2\cdot CH(OH)\cdot CMe_2\cdot OH$, b. p. 136—137°/81 mm.; (3) *di*iso*butylethylene glycol* [*βη-dimethyloctane-δε-diol*],

$$CHMe_2\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot CHMe_2,$$

m. p. 92°, which is formed in accordance with the equations:

$$CH_3\cdot COMe + CHMe_2\cdot CH_2\cdot CH_2\cdot OH = CHMe_2\cdot OH + CHMe_2\cdot CH_2\cdot CHO;$$

the latter

$$+ CHMe_2\cdot CH_2\cdot CH_2\cdot OH = CHMe_2\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot CHMe_2;$$

(4) resinous products not identified. T. H. P.

Photochemical Studies. V. Triboluminescence. JOH. PLOTNIKOW (*Prometheus*, 1919, **30**, 235—236; from *Chem. Zentr.*, 1919, iv, 462—463).—An apparatus is described with which triboluminescence can be excited under constant, comparable conditions. The triboluminiscope consists of a marble cylinder on which a thick glass plate is pressed, the pressure being regulated by two screws. The substance under investigation is placed between the

plate and the cylinder, and, on rotation of the latter, becomes ground at the point of contact. If the substance is triboluminescent, an illuminated band appears which shines continuously if the rotation is uniform. A special type of camera intended for use in photographing the band is also described. If the substances under investigation are hard enough to abrade the apparatus, the latter is formed from an agate cylinder and a quartz plate. For purposes of demonstration, the use of salophen, which gives a pale green triboluminescence, is recommended. H. W.

Relationship between the Range and the Life of α-Rays. F. KIRCHOF (*Zeitsch. physikal. Chem.*, 1919, **93**, 619—622).—It is shown that the range of the α-ray emitted by all radioactive elements is shorter the greater the life of the atom producing it. On plotting the range against the half-life, three similar curves are obtained, one for each radioactive family. On plotting the logarithms of the range against the logarithms of the half-life, curves are obtained which indicate that with a range, zero, the life is not infinitely large, but has a finite value about 10^{15}—10^{16} years. Applying this result to Ra-*G*, the author concludes that it is disintegrating at the above-named rate, but that its α-ray has no penetrating power. It is also deduced that the α-rays from isotopes have not the same range, but values corresponding with their own family. J. F. S.

The Radioactivity of Uranium. CHARLES STAEHLING (*Compt. rend.*, 1919, **169**, 1036—1039).—The oxides of uranium studied were obtained from different sources after careful purification and subsequent calcination either of uranyl nitrate or ammonium nitrate. The activities of such oxides were followed over the period from January 13th, 1913, to July 18th, 1914, and a further series of measurements were made in November, 1919. All the oxides studied showed a lowering in penetrating activity varying from 1 to 30·7%, and the curves indicate that half the lowering took place in 6·2 months. The lowering was greatest in the case of the green oxides and least with the black oxides. In the case of a blackish-green oxide, which showed a lowering from 5·95 to 4·64; when this oxide was dissolved in nitric acid and the nitrate again calcined, giving the black oxide, the activity rose again to 5·90. If then this oxide was converted into the green oxide by passage through ammonium uranate, it retained its high restored activity. Renewing the surfaces of the disks did not modify the activities observed. W. G.

Dependence of the Di-electric Constant of Gases on Temperature. HANS RIEGGER (*Ann. Physik*, 1919, [iv], **59**, 753—760).—The dielectric constants for air, hydrogen, methane, carbon dioxide, and carbon monoxide have been measured at low temperatures, and a series of pressures (200—760 mm.) by Mandelstam's dynamometer method (*ibid.*, 1910, **33**, 490). The

results are calculated to 760 mm. pressure in each case by the formula $(\epsilon_1 - 1)/(\epsilon_2 - 1) = \rho_1/\rho_2$, and the values for $\epsilon - 1$ found as follows: air (−185·5°), 0·001902; hydrogen (−191°), 0·000928; methane (−154°), 0·00216, carbon dioxide (−73°), 0·001392; carbon monoxide (−189°), 0·002633. The values are compared in all cases with those at ordinary temperatures (16—18·5°) and 760 mm. pressure. J. F. S.

The Theory of Electrolytic Ions. XI. The Limiting Values of Molecular Conductivity and their Determination. Richard Lorenz (*Zeitsch. anorg. Chem.*, 1919, **108**, 81—110).—The limiting value, μ_∞, of electrical conductivity can be calculated from the so-called Ostwald-Bredig rule, $\mu_\infty = \mu + \Delta$, where Δ varies with the dilution at which μ is observed. The values of Δ were determined empirically for the sodium salts of different acids and the chlorides of different bases by Bredig, and are given in his tables for dilutions from 32 to 1024. Two formulæ were given by Kohlrausch for calculating μ_∞, (1) for very high dilutions, $\mu_\infty - \mu = a[S_0]^{\frac{1}{2}}$, and (2) for less high dilutions, $\mu_\infty - \mu = b[S_0]^{\frac{1}{3}}$, in which $[S_0]$ is the concentration of the salt and a and b are constants. A statistical study of the data available for a very large number of organic cations of the ammonium type has now been made with the object of determining which of these formulæ gives the most reliable values of μ_∞. Both graphic and algebraic methods were used in applying the two Kohlrausch formulæ, and the values found for the constants a and b were practically the same by both methods. It was found that a and b are undoubtedly "universal" constants, since the deviations from the mean value show no relation to the constitution of the ions. The mean values are a, 91·54; b, 58·2. The values of Δ in the Ostwald-Bredig formula can be calculated from either of the above equations when the constants are known. When compared with the values given by Bredig, those obtained from the first equation show the best agreement, but this is no proof of their superiority. The two equations give slightly different values for μ_∞, but it is impossible to decide which is the more accurate. From the study of the data for a number of inorganic salts, it was similarly impossible to decide between the two formulæ. E. H. R.

The Theory of Electrolytic Ions. XII. The Limiting Values of Molecular Conductivity and Kohlrausch's Extrapolation Law. Richard Lorenz (*Zeitsch. anorg. Chem.*, 1919, **108**, 191—210. Compare preceding abstract).—For the determination of Δ from the relation $\mu_\infty = \mu + \Delta$, values of Δ are given in Bredig's tables for dilutions from 32 to 1024, these values being applicable to all sodium salts of univalent anions and all chlorides of univalent cations. Bredig's values for Δ were arrived at empirically, but they can be calculated from Kohlrausch's equation, $\mu_\infty - \mu = a[S_0]^{\frac{1}{2}}$. This calculation has been made for a large number of inorganic salts, the conductivities of which have been accurately

determiued, and when the values of Δ so obtained are compared with those given by Bredig, considerable disagreement is found. It is shown ou theoretical grounds that Bredig's rule is unsound; it gives only a rough approximation to the true value of μ_∞. A critical examiuation of Kohlrausch's conductivity measurements of inorganic salts shows that the formula $\mu_\infty - \mu = a[S_0]^{\frac{1}{2}}$ expresses the results with a high degree of precision for dilutions from 10,000 to 100, whilst from 100 to 10 the formula $\mu_\infty - \mu = b[S_0]^{\frac{1}{3}}$ is better. A more general expressiou is $\mu_\infty - \mu = A[S_0]^n$, where A and n are functions of the dilution. Whilst in the series of salts of univalent organic cations, the constants a and b of the above extrapolation formulæ retain the same value throughout the series (see preceding abstract), in the case of the inorganic salts of univalent cations the values of these constants increase with the atomic weight of the cation in a series such as that from lithium nitrate to cæsium nitrate.

E. H. R.

Conductivity. V. Measurement of the Conductivity of Solutions. H. I. Schlesinger and F. H. Read (*J. Amer. Chem. Soc.*, 1919, **41**, 1727—1732).—It is shown that although the minima obtained in the measurement of the electrical resistance of solutions may be perfectly sharp, nevertheless the results may be incorrect. This difficulty can be overcome by placing the telephone across the ends of the bridge wire and using an air condenser in parallel with the smaller capacity. It is also shown that the "cell-constant" ought to be determined from solutions which cover the whole range of resistance eventually to be measured. J. F. S.

Equilibria Across a Copper Ferrocyanide and an Amyl Alcohol Membrane. Frederick George Donnan and William Edward Garner (T., 1919, **115**, 1313—1328).

The Action Exerted by Antagonistic Electrolytes on the Electrical Resistance and Permeability of Emulsion Membranes. G. H. A. Clowes (*Proc. Soc. Expt. Biol. Med.*, 1918, **15**, 108—111).—The author brings forward various experimental data derived from electrical conductivity and permeability experiments with artificial emulsion membranes in support of his contention that variations in the permeability of the protoplasmic membrane are attributable to the action of electrolytes and metabolic products on delicately balanced interfacial soap films and emulsion systems and that proteins play no part in the valve-like mechanism controlling permeability other than to afford a supporting filamentous or mesh-like structure. In support of this it is further pointed out that when blood plasma is clotted by the addition of calcium chloride no considerable change in electrical resistance is noted, whilst in the transformation of an emulsion of oil in water into one of water in oil by shaking with calcium chloride the resistance suddenly rises to an enormous extent at the critical point at which oil becomes the continuous or external phase. This all fits in with the well known fact that alkalis, salts of sodium, potassium, etc.,

promote the permeability of tissues whilst salts of calcium, magnesium, and other bi- and ter-valent cations exert the reverse effect, also with the high potassium content and low calcium content of rapidly growing tumours and the reverse relation in slow-growing or stationary tumours. CHEMICAL ABSTRACTS.

Phenomenon after Anodic Polarisation. I. A. SMITS, G. L. C. LA BASTIDE, and J. A. VAN DEN ANDEL (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 82—88).—When the metals iron, nickel, and chromium are anodically polarised in solutions of their salts, using a current density of a definite value, and the potential measured after the polarising current has been broken, it is found that the potential passes through a minimum and then rises to the value before polarisation. Similar experiments with copper and silver did not produce the same effect, so that it appears this phenomenon is only shown in solutions where ions of two stages of oxidation exist or may exist. To test this point the experiment was repeated with iron, using a solution of ferrous chloride, which had been freshly boiled with iron powder, an atmosphere of hydrogen being used. The results show that the minimum potential is no longer observed, and that qualitatively, at least, iron behaves like copper and silver. J. F. S.

Potentials of the Zinc and Cadmium Electrodes. W. GRENVILLE HORSCH (*J. Amer. Chem. Soc.*, 1919, **41**, 1787—1800).—The *E.M.F.* of the following cells has been determined at 25°: $Zn|ZnCl_2|AgCl|Ag$; Cd(amalgam)$|CdCl_2|AgCl|Ag$; Cd(amalgam)$|CdCl_2|Cd$; and $H_2|HCl(0\cdot01N)|AgCl|Ag$. In the first cell the concentrations of zinc chloride solution varied from 0·0003*M* to 0·01*M*; in the second the concentration of cadmium chloride varied from 0·0001*M* to 6·61*M* (saturated). The normal electrode potentials of zinc and cadmium were found to be 0·758±0·002 volt and 0·3992±0·0010 volt respectively, the normal hydrogen electrode being taken as zero. The free energy of dilution of zinc chloride and cadmium chloride solution was calculated, and the following values obtained:

c_1.	c_2.	$F(CdCl_2)$.	$F(ZnCl_2)$.
0·1 *M*	0·01 *M*	1306 cal.	—
0·01 *M*	0·001 *M*	1615 cal.	1719 cal.
0·005 *M*	0·0005 *M*	1705 cal.	1858 cal.

J. F. S.

The Effect of Amalgamation on the Single Potential of Aluminium. LOUIS KAHLENBERG and JOHN A. MONTGOMERY (*Trans. Amer. Electrochem. Soc.*, **36**, 12 pp.).—The single potential of aluminium was measured in a $\frac{1}{3}M$-solution of aluminium chloride at the ordinary temperature. The highest value obtained with unamalgamated aluminium was 0·32 volt, and with amalgamated aluminium, 1·00 volt. The mercury removes the coat of resistant oxide. In the first few seconds after immersion the value

1·09 decreases rapidly to 1·04—1·07, owing to formation of oxide over the amalgam. It was shown that the potential measured is actually that of the aluminium, and not that of an aluminium amalgam. CHEMICAL ABSTRACTS.

The Potential Necessary for the Electrolysis of Solutions of Iron. W. ALBERT NOYES, Jun. (*Compt. rend.*, 1919, **164**, 971—973).—The minimum potential necessary for the electrolysis of a solution of a ferrous salt between electrodes of electrolytic iron is 0·66 volt at 20°; this value diminishes 0·007 volt for each degree rise in temperature up to 110° when it attains a minimum, and rises again with further rise in temperature. W. G.

Electrical Endosmosis of Molten Sodium Chloride in Carbon. WA. OSTWALD (*Kolloid Zeitsch.*, 1919, **25**, 115—116).—When molten sodium chloride is electrolysed between carbon electrodes there is scarcely any evolution of chlorine or formation of sodium unless special conditions are established, but the negative electrode increases in volume and is partly destroyed. On cooling and treating with water the electrode falls to powder, whereas the positive electrode is unaffected either during the electrolysis or on treatment with water. The behaviour is due to the cataphoresis of the molten sodium chloride. J. F. S.

Heusler's Alloys. O. VON AUWERS (*Zeitsch. anorg. Chem.*, 1919, **108**, 49—69).—The opinion was expressed by Heusler that the alloys of the aluminium–manganese bronze series owe their ferromagnetic properties to a compound of the form $(AlM_3)_x$, where M_3 represents an isomorphous mixture of manganese and copper. Whether the magnetism is to be attributed to simple molecules AlM_3, to complexes, or to a particular crystal lattice remained obscure. The phenomena attending the so-called ageing of these alloys have an important bearing on the constitution of their ferromagnetic constituent. The cast alloys have weak magnetic properties, and have to undergo the ageing process, that is, prolonged heat treatment at temperatures between 100° and 300°, to develop their full magnetic power. One effect of this treatment is to raise the magnetic transition temperature along a curve similar to a magnetisation curve. When magnetisation is plotted against time of ageing for different field strengths, a series of curves is obtained, of which those for lower field strengths show a sharp maximum with a subsequent fall to a constant magnetisation. In the curves for high field strengths the maximum is flattened out and the corresponding point is followed by a gradual rise in magnetisation as the time of ageing increases. The ageing process appears to involve two superimposed molecular changes. The author considers that at the magnetic transition point the magnetic particles become dissociated. On quenching from about 600° the alloy contains very few magnetic molecules. By slow cooling or by the ageing process the particles again become associated and the magnetisation and coercive force

both increase. With low field strengths the coercive force, that is, the intermolecular force, predominates over the magnetising force, and this explains the maximum in the above-mentioned curves. The highest point of the magnetisation curve is reached when the coercive force is a maximum, that is, when the maximum number of magnetic particles are present. The coercive force depends on the temperature of ageing, and reaches a maximum with temperatures from 190° to 260°. Above this temperature, it falls off rapidly, presumably because the dissociation of the particles has then commenced. E. H. R.

Some Fusion Curves, the Condition Diagram of Resorcinol and the Condition Diagrams of some Cryohydrates. WALTER DENECKE (*Zeitsch. anorg. Chem.*, 1919, **108**, 1—43).—The pressure–temperature fusion curves of betol, triphenylmethane, erythritol, guaiacol, salol, and benzoic anhydride, all substances of low crystallisation velocity, have been determined experimentally by Tamman's method, which consists in heating a quantity of the substance under pressure and plotting the temperature–pressure curve. When fusion commences, the curve changes direction owing to a rapid increase in pressure, and the ordinates of the poiut at which the change of direction starts give the temperature of the melting point and the corresponding pressure. From a number of such observations at different pressures the fusion curve is plotted. The apparatus used was that described by Tamman (Kristallisieren und Schmelzen, 1903, 195). In each case the curve can be represented by an equation of the form $t = t_{p=1Kg} + ap - bp^2$, in which a and b are constants and p is the pressure at the fusion point t. All the curves are smooth, and show no evidence of polymorphism in the substances examined, although betol, triphenylmethane, and erythritol are all known in two or more crystalline modifications.

The same experimental method was applied to the study of the transition between the two forms of resorcinol. The transition of pure resorcinol is extremely slow, but is accelerated by the addition of xylene. In presence of xylene, as the temperature is raised, the pressure begins to fall when the transition commences, the fall being most marked with 1% of xylene. The more xylene there is present, the lower the temperature at which the transition begins. Increasing pressure lowers the transition temperature, but also lowers the transition velocity.

To investigate the separation of different forms of ice from cryohydrate solutions, such solutions of sodium chloride, potassium chloride, ammonium chloride, sucrose and magnesium bromide were studied by cooling under pressures up to 3000 kilos. per sq. cm. down to about −70° and plotting the temperature–pressure curves. The regions of the equilibrium diagram of water in which the ice forms I, II, and III′ are stable were thus included. In the ice I field, this form generally separated, but once, from a sodium chloride cryohydrate solution, a form was obtained which appeared to be a less stable form of ice I, and twice, from a magnesium

bromide solution, a more stable form of this group separated. At pressures above 2400 kilos. ice III′ was always obtained from sodium chloride solutions, although this is the ice II region. From potassium chloride solutions sometimes ice II and sometimes ice III′ was obtained, and from ammonium chloride generally ice V. From sucrose solution ice III′ usually separated, but on one occasion a denser form, probably the most stable form of ice II, was observed. When ice I first separated and the pressure was raised subsequently, ice III′ was formed, except in the case of magnesium bromide, where the pressure was raised to 3000 kilos. without inducing transition into a denser form of ice. The position of the transition curve of forms I and III′ is not changed through the presence of the salts. The salts are therefore not appreciably soluble in these forms of ice.

E. H. R.

Vapour Pressures of Mercury in the Range 120—250°. ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1919, **41**, 1783—1787).—A method is described for the measurement of low vapour pressures, involving the use of two McLeod gauges, hot and cold respectively. The method has been used to determine the vapour pressure of mercury at 121·8°, 150·0°, and 191·5°. The following values are found in mm. of mercury: 121·8°, 0·829 mm.; 150·0°, 2·802 mm.; and 191·5°, 13·02 mm. It is shown that the equation connecting vapour pressure and temperature over the temperature range 250—453° (A., 1910, ii, 1037) may be employed without modification of its constants over the range 120—250°.

J. F. S.

Rectification by Adiabatic Condensation without Expansion. E. CHENARD (*Bull. Soc. chim.*, 1919, [iv], **25**, 546—552).—As a result of a series of distillations of alcohol–water mixtures through a special apparatus designed (1) to remove from the vapour any liquid transported in the vesicular state, (2) to effect a preliminary partial condensation of the vapour and collection of the condensed portion, it is shown that the law of correspondence between the strengths of liquids and vapours in contact, in a rational process of condensation, is almost identical with the law of fractionation by vaporisation. The process of enrichment of the vapour by means of partial condensation is capable of being very useful and also very simple in its working. Starting with a vapour containing 35% of alcohol, it was found possible by fragmentary condensation, in six stages, of about 54% of the initial weight, to obtain a vapour containing 64% of alcohol. At the same time, the six fractions would, on boiling, give vapours richer than the initial vapour.

W. G.

Distillation in a High Vacuum. J. HOUBEN (*Ber.*, 1919, **52**, [*B*], 1460—1462).—The principle of the method has already been described by Erdmann (A., 1904, ii, 20). A high vacuum is attained by means of an ordinary water pump through filling the

apparatus with carbon dioxide and condensing it in a suitable receiver by liquid air. The new improvement consists in letting the carbon dioxide enter in a continual stream through a fine capillary below the liquid, so as to prevent uneven boiling. A pressure of 0·12 mm. is easily maintained. J. C. W.

Comparative Investigation of the Efficiency of Still-heads of Various Types. J. Friedrichs (*Zeitsch. angew. Chem.*, 1919, **32**, 340—344).—In order to test the efficiency of different types of still-head, a mixture of equal quantities of benzene and toluene was distilled at a constant speed, which was controlled by means of a vapour pressnre regulator between the still-head and the condenser. The temperature within the still-head and the volumes of distillate were taken at regular intervals, and the results are given in tabular form. It was found that still-heads containing glass beads or fragments were the most effective, whilst for the distillation of larger quantities of liquid the use of a long tube, as in Hempel's apparatus, is best. Winssinger's modification of Hempel's still-head gives good results with liquids boiling below 100°, whilst a modification of Plücker's apparatus combines the advantages of Winssinger's dephlegmator and Ekenberg's rectifying apparatus. In the case of small amounts of liquids, Linnemann's apparatus gives the best results. [See also *J. Soc. Chem. Ind.*, 1919, 964A.] C. A. M.

Heat of Hydration of Gaseous Ions. K. Fajans (*Ber. deut. physikal. Ges.*, 1919, **21**, 549—558).—The heat of solution of a salt in water is regarded as made up of two quantities, (i) the heat absorption necessary for complete dissociation of the salt into gaseous ions, and (ii) the heat developed in the solution of these ions in water. The latter quantity is termed the heat of hydration of gaseous ions. From a knowledge of L, the heat of solution of a binary salt, and U, the total energy change, the author shows that the heats of hydration of the gaseous ions may be calculated. Employing this method, the following values, in kilogram cal. per gram-ion, are calculated: H^+, 362; Li^+, 210; Na^+, 203; K^+, 182; Rb^+, 173; Cs^+, 174; Tl^+, 182; Ca^{++}, 475; Cl^-, -23; Br^-, -32; I^-, -43. The values are claimed to be accurate within 6 units in the case of cations and 10 units in the case of anions. J. F. S.

Heat of Ionisation and Chemical Constitution. E. Oliveri-Mandalà (*Gazzetta*, 1919, **49**, ii, 176—180).—With a few exceptions, weak electrolytes exhibit heats of ionisation differing little from a mean value of 500 cal., and attempts have been made to explain the exceptional values by means of the chemical constitution of the electrolytes concerned. Thus, according to Bauer (A., 1897, ii, 546), the magnitude of the heat of ionisation may indicate the union of the hydrogen of an electrolyte to a nitrogen rather than to an oxygen atom, whilst Hantzsch employs it to diagnose

the presence in solution of a pseudo-acid, and Jones considers that anomalous heats of ionisation support his hydrate theory. Further, the high heats of ionisation shown by water and hydrofluoric acid have been explained as the result of a process of depolymerisation.

The author points out that the heat of ionisation, calculated from the heat of dissociation, depends on the other constants of the equilibria existing in solution and on the thermal effects of these equilibria, so that the magnitude of the heat of ionisation of a substance cannot serve as a physico-chemical means of investigating either intramolecular changes of electrolytes in solution or transformations of other character. The particular cases of a pseudo-acid and of hydrofluoric acid are considered, and an equation identical in form with, but different in signification from, that found by Lunden in the case of ammonia is derived (compare A., 1916, ii, 367). T. H. P.

Differences in the Heats of Combustion and in Other Properties of Isomeric Forms of Compounds of the Type Tartaric Acid-Mesotartaric Acid. E. Berner (*Tidskrift Kemi*, 1919, **16**, 97—110, 118—128).—The differences in the heat of combustion, density, solubility, and sublimation point were ascertained for the isomeric forms of tartaric acid, phenylglyceric acid, and hydrobenzoin. For the heat of combustion, the units in the following are kilo. cal. per gram-mol. The methyl ester was used in place of tartaric acid. Tartaric acid in the *meso*-form gave 623·2 Cal., in the *d*-form 621·8 Cal. Correcting for the difference in the heat of solution, the difference between these two is 2·6 Cal. Corresponding stereoisomeric forms of phenylglyceric acid (m. p.'s 122° and 141° respectively) gave 1011·2 and 1004·2 Cal., a difference of 5·4 Cal. after correcting for the heat of solution. In hydrobenzoin and *iso*hydrobenzoin the relations are reversed, the stereoisomeride corresponding with *i*-tartaric acid giving a smaller heat of combustion (1723·2 Cal.) than the other isomeride (1728·0 Cal.). The difference after correcting for the heat of solution is 4·5 Cal. *r*-Tartaric acid gave 0·5 Cal. more heat than did the *d*-isomeride. The author concedes that this may have been an experimental error, but cites Ossipoff (*Compt. rend.*, 1889, **109**, 475), who also noted a difference in the heats of combustion of these two isomerides, namely, 619·5 and 618·5 Cal. Attention is directed to the fact that the first four substances mentioned above are derived from the following acids, with heats of combustion as indicated: maleic (329·6), fumaric (320·7), *allo*cinnamic (1047·6), and cinnamic (1042·3 Cal.), respectively, and that in the transformation the relative rank as to energy is not altered. In isomeric forms greater solubility and lower m. p., sublimation point, density, and molecular volume in solution are associated with the isomerides of higher heats of combustion. The tartaric acids are an exception to this rule, as are also maleic and fumaric acids, from which the tartaric acid isomerides may be derived.

The Benzene [Formula] Problem. II. A. von Weinberg (*Ber.*, 1919, **52**, [*B*], 1501—1508).—From the data for the heats of combustion of various hydrocarbons, a discussion of the kinetics of benzene and related compounds is developed.

In the first place, it is shown that the heat of combustion of a saturated hydrocarbon, C_nH_m, can be expressed very nearly by the term $96n + 30m$ Cal., that is, each carbon and each hydrogen atom contributes a constant quantity. This is developed from two series of data. (1) Let x = the contribution of the carbon atom, and y that of the hydrogen. Then, in the case of ethane, $2x + 6y = 370{\cdot}9$, and in the case of propane, $3x + 8y = 526{\cdot}7$, whence $x = 96{\cdot}5$ and $y = 29{\cdot}65$. (2) The increment for the $\cdot CH_2$ group is known to be 156 Cal., and the average heat of combustion of the isomeric octanes is 1299·9 Cal. (Richard and Jesse, A., 1910, ii, 269). To the latter value should be added the latent heat of vaporisation, which is 8·09 Cal. Then $x + 2y = 156$ and $8(x + 2y) + 2y = 1308$, whence $x = 96$ and $y = 30$. Two consequences follow from this additivity. First, the energy of the rupture of a C·H linking must be the same as that of a C·C bond, and, secondly, the heat of combustion of a carbon atom in gaseous carbon must be the same as that of a carbon atom in a simple hydrocarbon vapour. Now it is quite remarkable that the above value, 96, is very nearly the same as the heat of combustion of solid carbon, from which it appears that in the vaporisation of carbon there is very little force of cohesion to overcome. This is in accordance with the view that carbon is mono-atomic in the diamond, as revealed by a study of the space-lattice and diminution of the specific heat at low temperatures.

The heat of dissociation of the C·H or C·C linking can be calculated as follows. The heat of combustion for one H in hydrocarbons is 30, but for two H atoms in hydrogen gas it is not 60, but 67·5, that is, the heat of dissociation of the C·H bond is less than that of H·H by 7·5. The value used by Nernst for the heat of dissociation of hydrogen is 100 Cal., from which it follows that the required quantity is 92·5 Cal.

The additional energy of the molecule due to one or more double linkings may be calculated by subtracting the value for the term $96n + 30m$ from the heat of combustion. From the values for ethylene, propylene, and hexylene, it appears that the increment due to the single ethylene linking is equivalent to about 30 Cal. For $\Delta^{\alpha\epsilon}$-hexadiene, however, it is only 16·3, instead of twice 30, and for ε-methyl-$\Delta^{\beta\epsilon}$-hexadiene it is only 20·8. This is due to the fact that the oscillations set up by one double bond interfere with and restrict those of the other. The case of the conjugated linkings is most interesting, for this really represents the energy of vibration of three pairs. Now if benzene has three conjugated double bonds, the energy of six oscillating pairs will have to be reckoned, that is, $2 \times 16{\cdot}3 = 32{\cdot}6$ Cal. Actually, the additional energy given out by benzene, above that calculated from the term $6 \times 96 + 6 \times 30$, is 32·7 Cal. if Roth's value for the heat of combus-

tion is correct (A., 1915, ii, 146), or 30·3 if Richards and Barry's number is accepted (*ibid.*, 421). The oscillation energy of each carbon atom in benzene is therefore 5·4 or 5·05 Cal., that is, about one-third of the energy of an ethylenic carbon atom. This agrees with the fact that the oscillation frequencies are slower in benzene and approach those of the visible spectrum. From the data available for naphthalene and anthracene, it appears that the average oscillation energy for one carbon atom is again about 5 Cal. Formulæ are given with which it is possible to discuss the amplitudes and frequencies of the oscillations of the α- and β-carbon atoms in these compounds.

The excess energy in the case of *cyclo*hexane, that is, the energy due to ring formation, is 8·2 Cal. This rises to 23·6 when one ethylene linking is also present (*cyclo*hexene), to 38·6 when two are present (*cyclo*hexadiene), but is 32·7 in the case of benzene.

J. C. W.

New Gas Pyknometer. K. KLING and L. SUCHOWEAK (*Metan*, 1917, **1**, 37—42; from *Chem. Zentr.*, 1919, iv, 437—439).—The authors describe a new form of gas pyknometer suitable for use with small quantities of gas and for the estimation of density without using a current of gas or a pump. The principle of the apparatus depends on the observation that carefully purified and dry mercury flows quantitatively from the well-cleaned apparatus. A single filling of the pyknometer by mercury suction leaves the vessel quantitatively filled with the gas. A further feature is the complete absence of stopcocks. The apparatus is very fully illustrated in the original.

H. W.

Table for the Correction of Volumes of Gases. WA. OSTWALD (*Zeitsch. angew. Chem.*, 1919, **32**, 359—360).—A calculation diagram for the correction of gas volumes to normal temperature and pressnre, including correction for the tension of aqueous vapour, may be constructed by plotting the values for barometer readings and the ascertained correction factors on two parallel logarithmic scales, joining the respective points on these scales by a straight edge and marking points between them to represent the corresponding temperatures. The temperature scale thus plotted includes the aqueous vapour correction, and will be found to take the form of a straight line parallel to the other two. The barometric and temperature scales can then be used for finding the corresponding correction factor without calculation, and the multiplication of the observed volume by this factor to obtain the corrected volume may be performed graphically, in the same manner by constructing two other logarithmic volume scales on the same diagram.

J. F. B.

Molecular Volumes. W. HERZ (*Zeitsch. anorg. Chem.*, 1919, **108**, 226—230).—For a number of homologous series of organic compounds, the author has compared the "true" molecular volumes given by the expression $V = D - 1/D + 2 \cdot M/d$, where D is the

dielectric constant and d the density, with the molecular volume at absolute zero, V_0 (A., 1919, ii, 220). In general, both V and V_0 increase with the molecular weight, although acetic acid shows an abnormally high value for V in the series of homologous acids. The molecular volumes at absolute zero are greater than the true molecular volumes, and the difference increases with the molecular weight. In the benzene series, the ratio V/V_0 is a constant, and the same is true in the paraffin series from hexane to decane. In the fatty acids, the alkyl formates, and alkyl acetates the ratio decreases as the series is ascended, but it approximates to a constant value in the higher members of each series. In the early members of these three series, the difference between the two molecular volumes is very small, indicating that the substances have a very compact structure. In the alcohol series, from methyl to amyl alcohol, the true molecular volume appears to be actually greater than the molecular volume at absolute zero. The abnormality becomes smaller with increasing molecular weight, and disappears beyond amyl alcohol. It is probably due to association in the alcohols, as a similar abnormality is found in the case of formic acid. E. H. R.

Molecular Volumes of Liquid Organic Compounds. HUGO KAUFFMANN (*Zeitsch. Elektrochem.*, 1919, **25**, 343—351).—The author has examined the molecular volumes of a large number of organic compounds, using the experimental data of Lossens (A., 1890, 323) for the purpose. It is shown that the molecular volume at the boiling point is not suitable for the investigation of regularities or for the calculation of atomic volumes. The molecular volume at a given temperature brings important regularities to light which run parallel with other physical properties. The density in homologous series of organic compounds approaches limiting values characteristic for each temperature: thus, at 0° D=0·8752; at 20° D=0·8616 as a limit. If the density of the first member of an homologous series is smaller than the limit, then the density in that series increases with increasing molecular weight, but should the density of the first member be larger than the limit then the density falls with increasing molecular weight in that series. The author recognises "Accumulation phenomena." This is the name applied to the combination of several groups or atoms with a given atom. Accumulation increases the molecular volume, and this mainly in the third and fourth stage. This is equally true for mixed and similar accumulation. Atoms or groups which bring about exclusively large increases in the molecular volume are termed *Eurogens*, and the accumulation phenomenon itself is termed *Eurogenism*. Carbethoxyl-, chlorine, nitro- and cyanogen groups are strong eurogens. The strength of the eurogens named increases in the order given; and other carbonyl-containing groups are stronger than the carbethoxyl group. The ethoxyl and phenyl groups are weaker than the carbethoxyl group, and the –CO·O– group is a bivalent eurogen. Of the alcohol radicles,

only the methyl group has eurogenic properties. This peculiarity of the methyl group has the effect that the second member of every homologous series shows a slight irregularity in the approach to the limiting value. The molecular volume of isomeric aliphatic compounds is controlled largely by the eurogenic character of the methyl group. In substituted derivatives the eurogenic influence of the methyl group is combined with its substitution influence. The difference between the molecular volumes of isomerides is a measure of the eurogenism. In accumulation of the second stage the methyl group may lose some of its activity, since methyl groups when they are combined with neighbouring carbon atoms, acting as accumulation centres, reduce the molecular volume. A similar state of affairs is shown to exist in silicon compounds where the silicon atom is acting as the accumulation centre. J. F. S.

A Thermodynamic Proof. ARRIGO MAZZUCCHELLI (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 47—51).—Lewis ["System of Physical Chemistry" (2nd Ed.), II, 140] directs attention to the divergent results attained by two proofs, both apparently unobjectionable, of the relation between pressure and equilibrium constant in dilute solutions. One of these proofs is due to Planck, who arrives at formula 220 of his "Thermodynamik" (3rd Ed.), and the other to Rice (*Trans. Faraday Soc.*, 1917, **12**, 318), who derives the formula $d/dP \log K = (V_1 - V_2)/RT$, where K is the equilibrium constant (constant of formation of the final system referred to concentration by volume) and $V_2 - V_1$ the variation in volume due to the integral transformation of the initial system into the final one. The author introduces certain modifications into Rice's system and shows that Rice's cycle then leads to Planck's formula, although he does not claim to have proved that such modifications are justified.

In the cases which up to the present have been subjected to experiment, a compression, besides altering the equilibrium constant in the sense favouring the system with a less total volume, that is, in accordance with the Le Chatelier–van't Hoff principle, also causes a certain increase in the concentration by volume, owing to the compressibility of the solution. Such increase in concentration, although without direct influence on the equilibrium constant, yet favours as a rule the system with the less number of molecules, of which it increases the relative quantity; in the experimental measurements, such increase figures, therefore, as a further variation of the equilibrium constant, and it should be taken into account by any rigorous theoretical formula. T. H. P.

Surface Tension and its Relationship to Other Properties of Liquids. W. HERZ (*Zeitsch. physikal. Chem.*, 1919, **93**, 607—612).—A theoretical paper in which the author examines the values of the surface tension, molecular surface energy, the temperature-coefficient of the molecular surface energy, and the molecular association of a number of organic compounds in their relations to the number of carbon atoms in the molecule. It is shown

that in homologous series the surface tension decreases with increasing number of carbon atoms, whilst the molecular surface energy becomes larger. The temperature-coefficient of the molecular surface energy increases in homologous series at the same temperature with the number of carbon atoms. From this it is deduced that the tendency to association decreases as the number of carbon atoms increases. Richard's rule that the compressibility is inversely proportional to the surface tension is examined in a large number of cases and confirmed. The compressibility is larger the fewer the molecules in unit volume, that is, the larger the molecular diameter. J. F. S.

The Technique of the Estimation of the Viscosity of Organic Colloids. E. Rothlin (*Biochem. Zeitsch.*, 1919, **98**, 34—92).—The superiority of the "capillary" methods over the "damping" methods in the estimation of the viscosity of fluids is discussed. The author examined the viscosity of various emulsoids under different pressures by means of Hess's viscometer (capillary principle). Emulsoids, like gum arabic, soluble starch, β gelatin, and casein, have been found to obey Poiseuille's law. Others like gelatin, egg-white, insoluble starch, agar, and soap have shown a deviation from the above-mentioned law as the pressure was diminished. In the case of one of these colloids, namely, gelatin, higher temperatures, the addition of hydrochloric acid, sodium hydroxide, sodium chloride of suitable concentrations as well as alcohol prevented this deviation. Two pressure regions in the viscosity of these emulsoids could be differentiated, the "upper" region, in which the colloids practically obeyed Poiseuille's law, and the "lower" region, in which they deviated from it. This deviation under low pressure the author attributes to the cohesive forces of the particles. The importance of the pressure factor and the dimensions of the capillaries in the estimation of the viscosity of fluids is pointed out. Hess's viscometer fulfils these requirements. S. S. Z.

Influence of the Red Blood Corpuscles on the Internal Friction of Blood. Karl Beck (*Kolloid Zeitsch.*, 1919, **25**, 109—110).—The viscosity of human blood has been measured with the object of ascertaining the relationship between this value and also of testing the Einstein relationship, $K' = K(1 + 2 \cdot 57)$ (*Ann. Physik*, 1906, **19**, 289; 1911, **34**, 591). It is shown that the α value depends on the number of suspended particles in the sense that at small concentrations the influence on the viscosity is smaller, and at high concentrations larger, than would be the case with a constant value of α (2·5). This is in keeping with previous results obtained for emulsions of oil (A., 1904, ii, 646; 1907, ii, 232). It follows, therefore, that the influence of a non-rigid particle on the viscosity cannot be determined either by Einstein's formula or by any simple application of the mixture rule. J. F. S.

Wo. Ostwald's Rule Connecting Colour and Degree of)ispersion. E. WEDEKIND and H. RHEINBOLDT (*Ber.*, 1919, 2, [*B*], 1794).—A note to remove a possible misconception of the uthors' views on Ostwald's theories (A., 1919, ii, 270).

J. C. W.

The Effect of Salts on the Vapour Pressure and Degree f Dissociation of Acetic Acid in Solution. An Experi- iental Refutation of the Hypothesis that Neutral Salts ncrease the Dissociation Constants of Weak Acids and lases. JAMES WILLIAM MCBAIN and JAMES KAM (T., 1919, **15**, 1332—1346).

Resolution of the Acid Salts of Dicarboxylic Acids into he Free Acids and the Normal Salts. JOH. PINNOW (*Ber.*, 919, **52**, [*B*], 1662—1667).—The method of estimating the first nd second dissociation constants of dibasic organic acids proposed y McCoy (A., 1908, ii, 466, 467), namely, by extracting solutions ; the acid salts with ether and determining the partition-coefficient : the acid, has been tested by Dieckmann and Hardt (A., 1919, , 326), who found that the ratio $k_1:k_2$ is not always independent ' the concentration, as it should be. They consequently formed ie opinion that there are sources of error inherent in the method self. Some of these are now discussed.

In the first place, the determiuation of the partition coefficient ›r the acid will be influenced by association and ionisation. As ie solution becomes more dilute, the associated molecules become :wer and the rate of extraction rises to a constant value (see A.,)15, ii, 679). Then it begins to fall nnless some sulphuric acid is ided to prevent ionisation. Another factor is the "salting out" fect of the normal and acid salts, which is, of course, less in dilute lutions than in concentrated ones. The question whether any of ie metallic salt is extracted by ether in the Partheil-Rose appara- is used in these investigatious has been tested in the case of sodium id potassium hydrogen oxalates and potassium tetroxalate but ie quantity is found to be quite negligible.

The relationship between free acid (*f*), acid salt (*m*), and normal lt (*d*), as expressed in the term $m^2/f \cdot d$, is independent of the iture of the alkali in the case of succinic acid. J. C. W.

Structure of the Capillary Layer. III. G. BAKKER (*Zeitsch. iysikal. Chem.*, 1919, **93**, 570—584. Compare A., 1915, ii, 614; 16, ii, 553).—The capillary layer is regarded as a film which has ›en formed by and between the liquid and gaseous phases without anging the total mass of these two phases. If n is the total imber of molecnlar layers of gas and liquid which go to form the pillary layer consisting of R new layers, then $R=qn$, where q is characteristic constant. Making use of the Laplace formula for olecular pressure, $Q=a/2(\sqrt[3]{\rho_1}+\sqrt[3]{\rho_2}) \cdot \sqrt[3]{M/N} \cdot (\rho_1-\rho_2)^2/H$ or $\sqrt[3]{\rho_1}+\sqrt{\rho_2}) \cdot \sqrt[3]{M/N} \cdot r_i(\rho_1-\rho_2)/1-T/a \cdot (dx/dt)$, in which a is

the Laplace constant, ρ_1 the density of the liquid, ρ_2 the density of the vapour, M the molecular weight, N the Avogadro number, H the surface tension, r_i the internal heat of vaporisation. Both formulæ are identical, since the equation $p = Tf(v) - a/v^2$ has been used in developing them. The equation for the number of layers in the capillary layer therefore becomes

$$R = 1 + Q/q + \sqrt{2Q/q + Q^2/q^2}.$$

If, however, the more exact formula of Clausius is used for the molecular pressure, $Q = \frac{1}{2}(\sqrt[3]{\rho_1} + \sqrt[3]{\rho_2})\sqrt{M/N} \cdot r_i(\rho_1 - \rho_2)/(1 - T/a \cdot da/dt) \cdot (1 + \beta\rho_1)(1 + \beta\rho_2)$. By means of these formulæ, the number of layers in the capillary layer, the thickness of the layer, and the number of molecular layers of vapour and liquid going in its formation have been calculated for carbon dioxide, benzene, and ethyl ether. The following values are obtained at the temperatures given:

Carbon Dioxide.

t	−25°	−10°	0°	10°	20°	28°	30°
R	4·8	5·4	5·4	6·9	8·8	13·3	28
n	4·3	5·0	5·1	6·6	8·6	13·2	28
ζ	2·6	2·9	2·9	3·7	4·8	7·2	15 $\mu\mu$

Benzene.

t	5·4	50°	80°	100°	150°	200°	250°	275°	280°
R	3·8	5·27	5·0	5·23	5·35	5·8	8·3	12·7	17·8
n	2·9	4·3	4·2	4·5	4·7	5·4	8·0	12·4	17·7

Ethyl Ether.

t	0°	20°	50°	80°	120°	170°	190°	193°
R	4·2	5·1	5·1	6·1	7·0	9·6	18·4	24·5
n	3·4	4·2	4·4	5·4	6·4	9·3	18·2	24·5

The present results are compared with, and criticised in connexion with, the results published in previous papers (*loc. cit.*).

J. F. S.

The Molecular Theory of Solution. Samuel Clement Bradford (*Phil. Mag.*, 1919, [vi], **38**, 696—705).—The theory of solution is considered from the point of view of the attractions of the solute and solvent particles for themselves and for one another. Whereas on Traube's "cohesion pressure" theory of solution, wherein cohesion pressure signifies the attraction of solute and solvent, the solubilities of organic liquids follow the order of their cohesion pressures, the solubilities of solid substances are in the reverse order. On the basis of the kinetic theory, the electronic theory leads to an expression of the form $f = M_w^2/r_w^4 - 2M_sM_w/r_{sw}^4 + M_s^2/r_s^4$, where M_w and M_s are respectively the moments of atomic doublets in solute and solvent, and r_w, r_{sw}, and r_s the respective distances between the centres of two solvent doublets, a solute-solvent doublet, and two solute doublets for the force initially tending to prevent solution.

This relation, combined with that expressing the ratio of the number of molecules in unit volume of the liquid solvent to the number in unit volume of the solid solute, is employed to deduce a number of conclusions relating to solution. Thus, the more a solute increases the surface tension of the solvent, the less its solubility. In the case of solutes which increase the surface tension of the solvent, the order of the compressibilities of their solutions will be the same as that of the solubilities of the respective solutes. Salts have a greater solubility, the larger their respective molecular volumes. It is shown that in accordance with the theory developed, the solubilities of sulphur dioxide, hydrogen sulphide, nitrous oxide, carbon dioxide, carbon monoxide, oxygen, nitrogen, and hydrogen are greater in alcohol than in water, and that, moreover, the difference of solubilities in the two liquids increases as the molecular cohesion of the gas diminishes. J. S. G. T.

Thermochemical Proof of Born's Crystal Lattice Theory. K. FAJANS (*Ber. deut. physikal. Ges.*, 1919, **21**, 539—548).—The author has calculated the energy of formation of gaseous ions from the crystalline salt by means of the known experimental values for the heat of solution of calcium chloride, calcium iodide, lithium iodide and chloride. These results are compared with the corresponding values calculated on the basis of Born's cubic atom model theory (A., 1919, ii, 188). It is shown that the two sets of values are in excellent agreement, and that they furnish a confirmation of this theory. J. F. S.

Colloid Synthesis by means of Oscillating Arcs. GÖSTA BÖRJESON and THE. SVEDBERG (*Kolloid Zeitsch.*, 1919, **25**, 154—158).—Using capacities in circuit, arcs of various metals have been struck in alcohol when the disintegrated metal forms colloidal solutions. In the experiments with a capacity of $12{\cdot}8 \times 10^{-8}$ *MF* and a current of 1·5 amperes colloidal solutions of antimony, lead, bismuth, zinc, gold, platinum, silver, copper, aluminium, and cadmium have been obtained. By this method the colloidal metal is produced more rapidly than by the earlier Svedberg method, in some cases four times as rapidly. The stability of the sols is fairly great, although a certain amount always separates, but even then the bulk of the metal remains in solution. Gold and platinum are exceptional, being very unstable. J. F. S.

The Effect of Organic Acids and their Amino-compounds on the Hydration of Agar and on a Biocolloid. D. T. MACDOUGAL and H. A. SPOEHR (*Proc. Soc. Expt. Biol. Med.*, 1918, **16**, 33—35).—Three groups of substances were selected: (1) succinic acid and its amino-compound, aspartic acid, both of which are dibasic, and its amide, asparagine, which is monobasic; (2) acetic acid and glycine, which are monobasic; (3) propionic acid and alanine, also monobasic, their action on the swelling of sections of agar and a mixture of 8 parts of agar and 2 parts of oat protein being

studied. Equimolecular concentrations of the three organic acid present small divergence of effect on agar and more positive differ ences in agar-protein. Agar swells more in succinic acid than in it amino-compound, but reverses this relation with the other two acid and their amino-compounds. The agar protein biocolloid showed greater hydration in the amino-acids than in the related organic acids, greater even than in distilled water. Glycine facilitates hydration in all concentrations above 0·01*M* in both agar and agar-protein, and also in agar-gelatin. The amide, asparagine, induces a maximal hydration, greater even than that possible in agar in distilled water and very high at all concentrations.

CHEMICAL ABSTRACTS.

Protective Colloids. 2nd Series. Cetraria Islandica as Protecting Colloid. IV. Colloidal Copper. A. GUTBIER and E. SAUER (*Kolloid Zeitsch.*, 1919, **25**, 145—153. Compare A., 1916, ii, 231, 303).—Extract of Iceland moss has been prepared in three ways: *A*, by extracting the moss with distilled water; *B*, by washing the moss first with dilute potassium carbonate and then extracting with water; *C*, the product *B* is rubbed with distilled water and then stirred with water and dialysed. These three extracts were used as protective colloids in the preparation of colloidal copper solutions from ammoniacal copper sulphate solutions and hydrazine hydrate. The copper sols are so very sensitive that it was possible to test the three extracts as to their protective action. Extract *C* is by far the most efficient, and *B* is far superior to *A*. The sols produced, using 0·1—0·05% of cetraria extract, are fairly stable, but deposit a dark red precipitate in fourteen days, which is reversible. Colloidal copper solutions which by transmitted light are clear red and slightly turbid by reflected light on keeping, deposit fine-grained, irreversible precipitates, but those which are bright red in both lights deposit completely reversible precipitates. The preparation of the solid colloid may be effected by adding ½—⅓ volume of alcohol. The colloids thus obtainable are not very rich in copper, the limit of absolute reversibility being reached with a copper content of 13·43%.

J. F. S.

Relationship between Shrinking and Diffusion Structure in Tanned (Hardened) Gelatin Jellies. W. MOELLER (*Kolloid Zeitsch.*, 1919, **25**, 101—109).—The structures of hardened jellies produced by shrinking and by the diffusion of solutions into the jellies have been investigated. It is shown that the structures, produced by the diffusion of solutions of sodium hydroxide into gelatin–sodium chloride jellies which have been hardened by formaldehyde, are due to changes in the internal structure of the micellar envelope. The thin, tanned layer attaches itself closely to the underlying coarse structure, and completely follows the direction of the coarser structure. Under tension, shrinkage lines appear in radial directions from the diffusion centre, and concentric ring systems are produced by the contractions of the micellar envelope.

rregularities may be caused by the passage of drops of alkali ydroxide solution through the fine pores of the surface film.

J. F. S.

Studies in Catalysis. Part XII. Catalytic Criteria and ıe Radiation Hypothesis. WILLIAM CUDMORE MCCULLAGH ƐWIS (T., 1919, **115**, 1360—1366).

Calculation of the Ammonia Gas Equilibrium. EDUARD ĮAUBER (*Zeitsch. anorg. Chem.*, 1919, **108**, 273—302).—A comarison is made of the results obtained for the nitrogen–hydrogen–ımmonia equilibrium at different temperatures and pressures by :aber and Le Rossignol and Jost (A., 1908, ii, 362, 761) respecvely. It is concluded that the results of these experimenters are ı full agreement, and further that the work of Jost, carried out ı Nernst's laboratory, was a sufficient scientific foundation for the ›chnical synthesis of ammonia.

E. H. R.

The Equilibrium between Carbon, Hydrogen, and Methane. :UBERT FRANK COWARD and STANLEY PIERCE WILSON (T., 1919, **15**, 1380—1387).

Calculation of the Temperature-coefficient of the Dis·ibution Ratio. F. H. MACDOUGALL (*J. Amer. Chem. Soc.*, 1919, **1**, 1718—1721).—A mathematical paper in which the author erives the temperature-coefficient of the distribution ratio for sucnic acid between water and ether. This value has previously been educed by Forbes and Coolidge (A., 1919, ii, 141), but the present ıthor points out that the mathematical expression is likely to be isleading. The present expression has the form $dR/dt =$ $'\sigma_s[(b_1+a_1n_2)/(1-a_1m_2)-R\,.\,(\beta_1+\alpha_1\nu_2)/(1-\alpha_1\mu_2)]$, which is idencal with that of Coolidge and Forbes. The Greek letters refer to ıe ether phase, and the Roman letters to the aqueous phase, σ_s is ıe mol. fraction of acid in water saturated with ether, $b_1 =$ $\text{im}(ds_1/dt)_{=e_1} e_1$, where e_1 is the mol. fraction of ether in the water ·yer, saturated with acid but not with ether, and s_1 is the mol. action of acid in the water layer saturated with acid but not with her; $n_2 = \text{Lim}(de_2/dt)_{s_1}$; the meanings of the other symbols follow ıe same order.

J. F. S.

Relations between Distribution Ratio, Temperature, and oncentration in System: Water, Ether, Succinic Acid. . S. FORBES and A. S. COOLIDGE (*J. Amer. Chem. Soc.*, 1919, **41**, '21. Compare preceding abstract, also A., 1919, ii, 141).—An :knowledgment of Macdougall's paper (*loc. cit.*) and an indicaon of the method by which a misinterpretation of the previous ɩuation may be avoided.

J. F. S.

The Propagation of Flame in Complex Gaseous Mixtures. Limit Mixtures and the Uniform Movement of Flame . such Mixtures. WILLIAM PAYMAN (T., 1919, **115**, ;36—1445).

The Propagation of Flame in Complex Gaseous Mixtures. II. The Uniform Movement of Flame in Mixtures of Air with the Paraffin Hydrocarbons. WILLIAM PAYMAN (T., 1919, **115**, 1446—1453).

The Propagation of Flame in Complex Gaseous Mixtures. III. The Uniform Movement of Flame in Mixtures of Air with Mixtures of Methane, Hydrogen, and Carbon Monoxide, and with Industrial Inflammable Gases. WILLIAM PAYMAN (T., 1919, **115**, 1454—1462).

The Ignition of Ether–Alcohol–Air and Acetone–Air Mixtures in Contact with Heated Surfaces. ALBERT GREVILLE WHITE and TUDOR WILLIAMS PRICE (T., 1919, **115**, 1462—1505).

The Diastatic Inversion of Sucrose: Influence of the Products of the Reaction on the Velocity of Hydrolysis. H. COLIN and (MLLE.) A. CHAUDUN (*Compt. rend.*, 1919, **169**, 849—852).—It has been shown previously (compare A., 1919, ii, 327) that the diminution in the velocity of inversion of sucrose by sucrase, due to an increase in the concentration of the sucrose, is really a linear function of the fluidity of the solution. It is now shown that the diminution in the velocity of inversion due to the presence of the products of inversion or of dextrose or lævulose separately is simply a physical effect due to an increase in the viscosity of the solution. In all these cases, the velocity of hydrolysis is a linear function of the fluidity of the solutions. W. G.

The Structure of Atoms. A. BERTHOUD (*Arch. Sci. phys. nat.*, 1919, [v], **1**, 473—496).—A résumé of recent work on this subject. W. G.

Modification of Bohr's Atomic Model. F. KIRCHOF (*Zeitsch. physikal. Chem.*, 1919, **93**, 623—633).—A theoretical paper in which the author puts forward an hypothesis of the constitution of the atom which, although based on Bohr's hypothesis, differs in many details. The outside ring is assumed to contain 8 electrons and atoms, and never more; thus, carbon and silicon contain 4 electrons and can combine with 4 atoms, fluorine and chlorine contain 7 electrons and may combine with 1 atom, argon contains 8 electrons in its outside ring, and so is saturated and cannot combine at all. This view is in keeping with Abegg's contravalency hypothesis, and it follows that the number of electrons in the outside ring is the same as the contravalency of the element. The author suggests that the second ring, from the nucleus, containing 8 electrons and beginning with sodium, is responsible for the K-series spectrum, whilst the L-series spectrum is due to a ring with 12 electrons (third from nucleus) and commences with zinc; the M-series spectrum is due to a ring (fourth from the nucleus) containing 14 electrons and commencing with gold. J. F. S.

No. 132

Spectroscopic Proof of Electrical Fields on the Surface of Chemical Atoms. J. STARK (*Ann. Physik*, 1919, [iv], **60**, 196—200).—A theoretical paper in which, from a consideration of the third subsidiary series of lithium and helium, and of the conditions under which these series become visible, it is shown that electric fields are situated on the surface of the atoms. J. F. S.

Nature of the Forces between Atoms in Solids. RALPH W. G. WYCKOFF (*J. Washington Acad. Sci.*, 1919, **9**, 565—592).—A theoretical paper in which the structure of the atom is discussed with reference to the nature of the forces operating between atoms; it is emphasised that only the arrangement of the outside electrons has a bearing on the phenomena usually described as chemical. The arrangement of the inner electrons cannot be deduced from chemical data alone. The outstanding fact is the tendency to form "closed clusters" of 8 or 16 electrons. A number of typical compounds are considered with reference to the nature of the forces producing them. All compounds lie between the two extremes of "polar" and "non-polar" compounds. A simple method of representing the type of combination in a given compound is put forward. Solid substances are classified, according to the nature of the forces of combination, into molecule-forming, polar, and valency compounds. The phenomena of adsorption, solubility, ionisation in solution, formation of complex ions, and molecular complexes are discussed from this point of view. J. F. S.

Derivation of Chemical Relationships from the Electron Theory. HEINRICH TRUDT (*Zeitsch. anorg. Chem.*, 1919, **108**, 137—160).—In a previous paper (A., 1919, ii, 330) was outlined a theory of the periodic system of the elements based on certain assumptions regarding the mode of arrangement of the electrons in the atoms. This theory is now extended to a consideration of the combination of atoms to form molecules and compounds. Since the inner electrons rotate in a series of rings as near to the equator of the atom as possible, it follows that the positive lines of force due to the positive charge of the nucleus are concentrated at the poles of the atom and attract valence electrons to this region. Combination between atoms therefore takes place at the poles of the atoms, and the electrons held in common between the combining atoms rotate in an orbit between the poles of the combined atoms. In addition to the attractive force between the valence electrons and the positive nucleus of opposing atoms, forces of attraction between the electrons of the inner rings and the positive spaces between them also come into play, and it is shown that, in the case of two atoms of a metalloid element, the net result is an attraction, whilst with two atoms of a metal a repulsion results, or a much weaker attraction. This explains why metalloids generally form polyatomic molecules, whilst the molecules of the metals are monatomic. Similar considerations explain the stability of compounds of different metalloid elements and the ionisation of salts

of the lithium fluoride type. The cause of odour in chemical compounds is traced to the oscillations of the valence electrons in their orbits between the poles of combined atoms. E. H. R.

Mathematical Proof that the Atomic Weights are Integers when O = 16. HAWKSWORTH COLLINS (*Chem. News*, 1919, **119**, 247—248).—When the elements are written down in ascending order of atomic weight, it is found that, of the first 25, 21 have values assigned to them which differ by less than 0·5% from integers. The probability that this has happened by accident is 1 in a billion. The five exceptions to this are: Gl = 9·1, Mg = 24·32, Ne = 20·2, Si = 28·3, and Cl = 35·46. Of these, neon need not be considered, because it is probably a mixture. If the atomic weights of the remaining elements are reduced by the same proportion, they become Gl = 9·00, Mg = 24·00, Si = 28·00, and Cl = 35·00. The atomic weights are dependent on that of chlorine, so that an error in chlorine would affect the others in the same way. The probability that this is due to an accident is 1 : 100,000. The author therefore draws the conclusion that all atomic weights are integers when the standard O = 16 is adopted. J. F. S.

Is the Ratio of the Atomic Weights O = 16 : Ag = 107·88 Correct? ALOIS BILECKI (*Zeitsch. Anorg. Chem.*, 1919, **108**, 113—118).—It has been shown (A., 1917, ii, 197) that the atomic weights of silver, 107·88, bromine, 79·991, and chlorine, 35·46, are multiples of the number $n_1 = 0·307350427$. Thus, $Ag = 351n_1$, $Br = 260n_1$, and $Cl = 115\frac{3}{8}n_1$. On the other hand, the atomic weights of oxygen and other elements determined with reference to oxygen are multiples of the number $n = 0·3076923$ that of oxygen being $16 = 52n$. An examination of the published determinations of the atomic weight of manganese shows that, when this is determined from ratios involving the halogens and silver, for example, $2Ag : MnBr_2$ or $2AgCl : MnCl_2$, the number 54·932 is obtained, which is practically equal to $178\frac{3}{4}n_1 = 54·9388$. When, however, the atomic weight is determined from the analysis of the sulphate, that is, from such ratios as $MnSO_4 : MnO$, $MnO : 4O$, the number 55·0 is obtained, which is equal to $178\frac{3}{4}n$. In the case of zinc, also, similar differences are shown between the atomic weights determined with respect to halogens on the one hand and oxygen on the other. It is suggested, on account of these considerations, that, if the atomic weight of silver is taken as 107·88, that of oxygen should not be 16, that is, $52n$, but $52n_1$, that is, 15·982. In the same way, the atomic weight of sulphur should be 32·026 instead of 32·06. E. H. R.

The Derivation of Valency Laws. The Principle of Cationic and Partial Valencies. HUGO KAUFFMANN (*Ber.*, 1919, **52**, [*B*], 1422—1435).—See this vol., i, 50.

Periodic Precipitates. The late LORD RAYLEIGH (*Phil. Mag.*, 1919, [vi], **38**, 738—740).—Periodic precipitates are best demon-

strated as follows. A glass lantern-slide is carefully cleaned and placed absolutely level. To 5 c.c. of a 10% solution of gelatin, one drop of a concentrated solution of sodium arsenate is added, and poured over the plate while hot. When it is quite set, bnt before it cau dry, a drop of silver nitrate solution containing a trace of nitric acid is allowed to fall on the plate. A series of rings of periodic precipitates of silver arsenate is obtained by this procedure. *The greater the concentration of the diffusing solution*, the closer the rings are together. The periodicity is supposed to originate from the difficulty of precipitation without a nucleus. One ring having been formed, precipitation occurs thereat until the silver nitrate solution has diffused to a place where a sufficiency of sodium arsenate solution remains to render possible new precipitation. The interval between successive rings increases with increase of distance from the centre of diffusion. Periodic structure is also exhibited when a few drops of a cold saturated solution of copper sulphate and salicin to which is added 3% of strong syrup (sugar) are spread on a microscope slide and warmed, excess of liquid being removed, and the plate kept at about 17° above the ordinary temperature until crystallisation sets in, and then cooled. A polarising microscope reveals a structure periodic some thousand times per centimetre. J. S. G. T.

History of the Discovery of the so-called Liebig's Condenser. R. A. (*Parfumerie Moderne*, 1919, **12**, 10—12; from *Chem. Zentr.*, 1919, iii, 209).—The discovery of the counter-current principle in condensers is not attributable to Liebig, but was made independently by a Frenchman, whose name is unknown, in the year 1770, by Christian Weigel in 1771, and by a Finn, Jean Gadolin. H. W.

Filter Funnel. ERICH LEHMANN (*Chem. Zeit.*, 1919, **43**, 726).—The stem of the funnel is divided so as to form two narrow channels; the part counecting the upper portion of these two channels forms a support for the point of the filter paper contained in the funnel. W. P. S.

Method for Rapid Filtration. J. DOCTERS VAN LEEUWEN (*Chem. Weekblad*, 1919, **16**, 1424—1425).—The author has obtained satisfactory results with the method proposed by Noyes (*Int. Sugar J.*, May, 1919; from *Chem. Anal.*), in which, by tearing off a corner from one or two thicknesses of the folded filter paper, an unbroken stream of liquid is obtained in the stem of the funnel, filtration being thereby accelerated. W. J. W.

Tait Vortex-rings and Colloidal Sulphur: with Lecture Experiments. I. GUARESCHI (*Atti R. Accad. Sci. Torino*, 1917–1918, **53**, 321—334).—Vortex-rings of mixed air and ammonium chloride vapour are so stable that they are able to traverse successively several layers of water or other liquid, the conclusion drawn by the author being that the ammonium chloride is present

in the colloidal condition. Good rings are also obtainable by forcing sulphur trioxide or phosphoric oxide vapour, by squeezing a rubber bulb, through a U-tube containing water, etc.; the orifice through which the rings issue may be either circular or square. Various procedures are described for obtaining rings by passing the above vapours, mixed with other vapours and gases, through different substances.

When hydrogen sulphide and air are passed together through a U-tube containing either fresh soda-lime or a mixture of quicklime and yellow mercuric oxide, *vivid incandescence is observed at a* certain point in the U-tube. In the latter case, when the resultant mixture of hydrogen sulphide and sulphur dioxide is passed through water, the latter becomes milky owing to the deposition of colloidal sulphur, which is precipitated in arborescent formation and falls from the surface to the bottom of the liquid in spirals, each of which is terminated by a ring similar to the vortex-rings. A modification of this experiment, for use as a lecture demonstration, is described. T. H. P.

Soluble Aluminium Phosphate. A Lecture Experiment. OLOF SVANBERG (*Zeitsch. anorg. Chem.*, 1919, **108**, 70—72).—When to a 1% solution of aluminium chloride, neutralised with ammonia if it has a slight acid reaction, are added a few drops of a 1—2% solution of potassium dihydrogen phosphate, both being coloured yellow by the addition of a drop of methyl-orange solution, the colour of the mixture immediately becomes red without the formation of any precipitate or of any turbidity. When the solution is warmed a precipitate comes down, but there is no further colour change. Measurements were made of the hydrogen-ion concentration in binary solutions of the two salts, and it was found that a maximum occurs with about 40 mols. % of potassium dihydrogen phosphate. Salts of calcium, magnesium, zinc, or cadmium do not give the colour change with the phosphate. Glucinum sulphate does give the reaction, but it is much more sensitive to excess of phosphate. E. H. R.

Inorganic Chemistry.

Preparation and Testing of Hydrogen of a High Degree of Purity. JUNIUS DAVID EDWARDS (*J. Ind. Eng. Chem.*, 1919, **11**, 961—963).—An apparatus has been devised as a substitute for the Kipp generator. It consists of two connected cylinders, into one of which the zinc is introduced, whilst a tube through a rubber cork in the bottom is connected with the acid flask. The outlet tube has a side connexion, which dips into mercury and serves as a pressure indicator and as a safety valve. Air is exhausted from the cylin-

ders, the acid flask nearly filled with dilute sulphuric acid, and a few fragments of zinc introduced to sweep out the air before the flask is attached to the cylinders. The acid is drawn up into the generator by turning a tap at the top and opening a vent in the stopper of the acid flask. Pure hydrogen is thus at once obtained and fresh acid introduced without admitting air. Tests made in comparison with pure electrolytic hydrogen by means of the interferometer (A., 1915, ii, 478) showed that hydrogen produced by this apparatus contained less than 1 part in 10,000 of impurities. In similar tests of the gas produced by a Kipp generator 83·86% of hydrogen was found to be present seventeen minutes, and 99·97% forty-two minutes after starting. [See also *J. Soc. Chem. Ind.*, 1920, 19A.] C. A. M.

New Experiment to Demonstrate the Minute Mass of a Hydrogen Atom. FR. BÜRKI (*Helv. Chim. Acta*, 1919, **2**, 703—704).—A yellowish-green fluorescence is distinctly observable in a darkened room when a beam of light is passed through 0·5 c.c. of a solution prepared by dissolving 0·4 mg. of fluorescein in 10 litres of water. The total quantity of hydrogen which can be furnished by the weight of fluorescein present in this solution is 6×10^{-11} grams, which therefore gives an upper limit for the mass of the hydrogen atom. The figure is greatly in excess of the generally accepted value. H. W.

Composition of the Atmosphere. AUGUST KROGH (*Math. fysiske Meddelelser*, 1919, **1**, No. 12, 1—19).—Our knowledge of the composition of the atmosphere is still quite uncertain, especially in regard to hydrogen and the relation between oxygen and nitrogen. Until very recently little attention has been paid to the variation in the mixture composing the atmosphere at different altitudes. Wegener claims that at a height of 70 km. hydrogen must be the chief constituent of the earth's atmosphere. Benedict has shown by 200 analyses extending over a period of nine months that the percentage of oxygen at the surface or laboratory level never varied more than ±0·01 from the average, and that of carbon dioxide never more than ±0·005. The author describes a new gas analysis apparatus with three gas burettes, one for moving the air sample to and from the absorption pipettes, and for saturating the air with moisture, a second convenient in size for measuring the air before and after the absorption of carbon dioxide, and a third which holds the residual gas after the absorption of oxygen. The author discusses general means for reaching more accurate and constant results. The heated platinum wire method has been applied for the detection of combustible gases, and the conclusion is drawn that hydrogen or other combustible gas is present in an amount which is probably less than 0·002%. The percentage of carbon dioxide in the streets of Copenhagen is usually increased by 0·001—0·007. The need of a thorough research to establish the absolute average composition of pure atmospheric air with more certainty and a study

of its variations, especially in the higher strata of the atmosphere, is strongly urged. Accurate analyses of samples taken simultaneously from aeroplanes at various heights up to 5 or 6 km. would give valuable information in regard to mixing by vertical currents. Automatic sampling by balloons is suggested. Up to the present time the absolute composition of atmospheric air at the earth's surface has been found to be CO_2, 0·030%; N_2, 79·022%; and O_2, 20·948%. CHEMICAL ABSTRACTS.

Nitrogen Generator for Laboratory Use. W. L. BADGER (*J. Ind. Eng. Chem.*, 1919, **11**, 1052—1053).—A wide-necked 2-litre bottle is closed with a rubber stopper through which passes one end of a Liebig condenser jacket (without the condenser tube); the lower water inlet is sealed off, and the upper one is connected with a side-tube which extends through the stopper to the bottom of the bottle. A bulb with delivery tube is sealed on the upper end of the jacket. The bottle is packed with copper wire, and as much ammonia (1:1) saturated with ammonium chloride is poured in as the bottle will hold. The jacket is filled with copper turnings. Air is blown in through a tube reaching nearly to the bottom of the bottle; the oxygen is absorbed rapidly, and practically pure nitrogen escapes from the delivery tube. The passage of the air (or nitrogen) causes the solution to circulate slowly up the jacket and through the side-tube into the bottle again. W. P. S.

The Synthesis of Ammonia at Very High Pressures. GEORGES CLAUDE (*Compt. rend.*, 1919, **169**, 1039—1041).—Having previously shown the possibility of using very high pressures for industrial purposes (*ibid.*, 649), the author has studied the synthesis of ammonia at these high pressures, and finds that at a pressure of 1000 kilos./cm.^{2} and at a temperature of 536° the yield of ammonia is over 40%. The zone of temperature within which this reaction takes place at a reasonable velocity under such a high pressure is 500—700°. W. G.

Behaviour of the Hydronitrogens [Nitrogen Hydrides] and their Derivatives in Liquid Ammonia. VI. Electrolytic Nitridation of Various Anodes in a Solution of Ammonium Trinitride. A. W. BROWNE, M. E. HOLMES and J. S. KING (*J. Amer. Chem. Soc.*, 1919, **41**, 1769—1776. Compare A., 1911, ii, 1084, 1085; 1913, ii, 583).—Solutions of 1 gram of ammonium azide in 36 c.c. of liquid ammonia were electrolysed at −67°, using anodes of copper, silver, cadmium, aluminium, lead, antimony, iron, and nickel. The gas evolved at both anode and cathode was measured, and the loss of weight of the anode determined. It is shown that copper anodes undergo electrolytic corrosion to an extent indicating the formation of some cuprous azide, CuN_3, with cupric azide, CuN_6, as the main product. No gas was liberated at the anode. With silver, cadmium, lead, and antimony anodes the corrosion resulted in the formation of normal azides,

AgN_3, CdN_6, PbN_6, and SbN_9, without liberation of gas at the anode. Aluminium, iron, and nickel anodes undergo corrosion, accompanied by the liberation of nitrogen. The aluminium anode became coated with a bulky pyrophoric scale of varying colour and texture. Deep red ferric azide, FeN_9, was obtained in solution when an iron anode was employed, but this product was ammonolysed and yielded an ammono-basic ferric azide. A pink deposit was formed on the nickel anode, presumably an ammono-basic nickel azide. J. F. S.

Some Properties of Nitrogen Trioxide, Pure or in Solution in Nitrogen Peroxide. GEORGES BAUME and MARIUS ROBERT (*Compt. rend.*, 1919, **169**, 968—970).—The authors have studied the melting-point and vapour-pressure diagrams of the system nitrogen trioxide–nitrogen peroxide. The melting-point diagram is normal, and has a single eutectic in the neighbourhood of the freezing point of pure nitrogen trioxide. From the vapour-pressure curves between $-80°$ and $35°$, the author deduces tbe b. p. of pure nitrogen trioxide to be $-27°/760$ mm.

Pure nitrogen trioxide can only exist at very low temperatures in the solid state or in the liquid state under pressure of nitric oxide. At temperatures above $-100°$ it dissociates. It is not possible to distil it in a vacuum because of the immediate formation of an atmosphere of nitric oxide at temperatures at which distillation is possible. W. G.

Silicon Hydrides. VII. Protosiloxane, $O:SiH_2$. ALFRED STOCK and KARL SOMIESKI (*Ber.*, 1919, **52**, [*B*], 1851—1860. Compare A., 1918, ii, 111).—In the earlier paper it was shown that dibromomonosilane reacts with water to form polymerides of protosiloxane, $O:SiH_2$. The unimolecular form has now been obtained as a gas by the action of the required amount of water vapour on dichloromonosilane in a very large flask under greatly reduced pressure. It has an extraordinary tendency to polymerise, much more so than the analogous carbon compound, formaldehyde, in consequence of which the flask must be perfectly clean and smooth. Liquid and solid polymerides are formed immediately on condensation. The liquid ones are like benzene, and can be obtained conveniently as a solution by shaking a benzene solution of dichloromonosilane with water. These benzene solutions are fairly stable towards water, but reduce silver nitrate in the cold. They correspond roughly with $(SiH_2O)_6$. The solid polymerides are insoluble. All the polymerides react with sodium hydroxide according to the equation $SiH_2O + 2NaOH = Na_2SiO_3 + 2H_2$. J. C. W.

Constitutional Formulæ of Kaolinite and other Silicates. RUDOLF WEGSCHEIDER (*Zeitsch. Elektrochem.*, 1919, **25**, 352).—It is shown that the constitutional formulæ of polysilicates must be written with the silicon atoms joined through oxygen and not directly with one another. Compounds with the silicon atoms directly united are reducing agents and unstable. Further, if the polysili-

cates are *considered* as *having* the silicon atoms directly united it will follow that the oxygen atoms must also be directly united, which again will point to instability. The combination of a strongly reducing group, –Si–Si–, with a strongly oxidising group, –O–O–, will, of necessity, give a compound of an extremely unstable character, which is certainly not the case with the polysilicates. [See also Simmonds, T., 1904, **85**, 681; Pukall, A., 1910, ii, 780; Manchot, A., 1910, ii, 1060.] J. F. S.

Theory of Binary Mixtures. V. Vapour Pressure and Molecular Constitution of Liquid Argon and Argon-Nitrogen Mixtures. F. DOLEZALEK (*Zeitsch. physikal. Chem.*, 1919, **93**, 585—595. Compare A., 1916, ii, 132).—A theoretical paper, in which, using the experimental data previously published, the association constants are calculated from the saturation pressure of the mixture, and also the molecular constitution of the mixtures and pure argon, the saturation pressures of the liquid mixtures and the constitution of the vapour. It is shown that liquid argon is partly composed of diatomic molecules and has an association constant at 85·11° abs. of $K=0{\cdot}20$. Hence at low temperatures argon possesses chemical affinity, and consequently argon compounds are to be expected at low temperatures. There is therefore no fundamental difference between the inactive gases and other gases, but only a difference of degree. When liquid argon is diluted with liquid nitrogen the diatomic molecules dissociate according to the law of mass action. The vapour tension of liquid argon–nitrogen mixtures, as well as the constitution of the vapour, may be calculated at all concentrations by means of the author's theory of solution (A., 1909, ii, 22). J. F. S.

Preparation of Metallic Potassium. FRITZ C. WICKEL and WALTER LOEBEL (D.R.-P. 307175; from *Chem. Zentr.*, 1919, iv, 361). —Accurately measured quantities of metallic sodium and potassium hydroxide are melted together with exclusion of air, so that sodium oxide is formed and potassium is volatilised from the mixture (at about 670°), and suitably condensed. Hydrogen is obtained as by-product. The process is suitable for the manufacturing scale. H. W.

The Autoxidation of Sodamide. HANS SCHRADER (*Zeitsch. anorg. Chem.*, 1919, **108**, 44—48).—The amides of the alkali metals are known to undergo autoxidation, with the formation of nitrite, hydroxide, and ammonia. When finely divided sodamide is exposed to air in presence of a little water, a yellowish-red oxidation product is formed, which is now shown to be a peroxide, probably of the formula $NaNH_2,O_2$. The peroxide formed was estimated by adding the product to a cold saturated solution of barium chloride, when barium peroxide was precipitated, and was estimated in the usual way. It was found that a sample of sodamide gave in fifty-eight days at ordinary temperature 0·44

mol. % peroxide and 6·9% nitrite. In dry air, autoxidation does not take place at the ordinary temperature, but at 100° to 110° the peroxide is slowly formed. The peroxide is stable in dry air, but in moist air is changed into a white substance, the aqueous solution of which gives the peroxide reaction. E. H. R.

Solubility and Fusion Relations at High Temperatures and Pressures. GEORGE W. MOREY (*J. Eng. Club, Philadelphia*, 1919, **35**, 509—519).—An address. The preparation of the compounds *monopotassium aluminate*, K_2O,Al_2O_3, large, octahedral crystals, and *monopotassium ferrite*, K_2O,Fe_2O_3, large, red, octahedral crystals, decomposed by water below 500°, is mentioned. CHEMICAL ABSTRACTS.

The Properties of Ammonium Nitrate. I. The Freezing Point and Transition-temperatures. REGINALD GEORGE EARLY and THOMAS MARTIN LOWRY (T., 1919, **115**, 1387—1404).

Action of Bromine on Calcium Carbide. EDWARD BARNES (*Chem. News*, 1919, **119**, 260—261).—Liquid bromine acts slowly on calcium carbide at ordinary temperatures, producing carbon hexabromide and calcium bromide. 4·5 Grams of finely powdered calcium carbide, treated with 45 grams of purified dry bromine in a 50 c.c. bottle for five months, gave a product which, after removal of excess of bromine, weighed 32·4 grams and contained 22 grams of hexabromoethane, 8·8 grams of calcium bromide, and 0·2 gram of unchanged calcium carbide. Calcium carbide and bromine heated in sealed tubes at 100°, until no further action was apparent, produced carbon and calcium bromide. Dry chlorine was found to have no action on calcium carbide exposed to it at the ordinary temperature for two months. S. S. A.

Reduction of Barium Nitrate by the Alternating Current. P. WENGER and A. LUBOMIRSKI (*Ann. Chim. anal.*, 1919, [ii], **1**, 339—342).—With lead electrodes, the yield of nitrite increases with the amperage, but with mercury electrodes the maximum yield is obtained with 0·6 ampere; the yield also increases with temperature in the case of lead electrodes, and decreases with aluminium or zinc electrodes. Temperature has little, if any, effect when copper, cadmium, or magnesium electrodes are employed. The oxygen liberated from the nitrate combines with the electrode, forming suboxides (copper, mercury, cadmium, and tin electrodes), hydroxides (lead, zinc, aluminium, and magnesium electrodes), or oxides (nickel and silver electrodes). The nitrate is not reduced by the metallic electrodes unless the current is passing. W. P. S.

Purification of Magnesia. Conditions in which Periclase or Crystalline Magnesia is Formed. J. MEUNIER (*Bull. Soc. chim.*, 1919, [iv], **25**, 560—562).—Magnesium oxide may be freed from contained calcium by igniting the material at a red heat and

subsequently, after cooling, extracting it with successive quantities of a 10% sucrose solution until the last extract does not give any turbidity with ammonium oxalate. If such material is then washed with water, dissolved in hydrochloric acid, the solution evaporated to dryness, and the residue gradually heated in a covered crucible until it attains a red heat, magnesium oxide is obtained in the form of crystals of periclase on the lid and sides of the crucible and on the surface of the amorphous oxide in the crucible. The material so obtained is very pure. W. G.

Concentrated Thallium Amalgams: their Electrochemical and Thermochemical Behaviour; Densities and Freezing Points. THEODORE W. RICHARDS and FARRINGTON DANIELS (*J. Amer. Chem. Soc.*, 1919, **41**, 1732—1768).—The electromotive force, density, specific volume, specific heat, heat of dilution, and freezing point of thallium amalgams up to a concentration of 40·9% thallium have been experimentally determined. The heat of solution of thallium in mercury and in various amalgams has also been determined. The *E.M.F.* measurements were made at 20°, 30°, and 40°, and are shown to be much greater than demanded by the simple concentration law. The temperature-coefficients of the *E.M.F.*'s have been calculated for the various amalgams, and they are found to be less than is demanded by the gas law and vary as the concentration increases. The solution volume of thallium is remarkably constant, varying only from 17·47 to 17·51, but it is somewhat larger than the specific volume (17·21) of thallium. Thallium, therefore, must expand on amalgamation. The coefficients of expansion were calculated from these results, and found to diminish with increasing concentration. The heat capacities were found to be distinctly larger than the sum of the heat capacities of the thallium and mercury in the amalgam. This excess is greater in dilute than in concentrated amalgams. The heat of dilution with mercury was determined at 20°, and from the results the values at 30° and 325° were calculated. Although the heat of dilution of thallium amalgam is a very different effect from the transfer of thallium from one amalgam to another, it is shown that either of these effects may be calculated from the other. Within the limits of experimental error, the heat effects in the cells of which the *E.M.F.* was measured may be calculated from either the heat of dilution of the amalgams, or the heat of solution of thallium in the amalgams, or the temperature-coefficient of the *E.M.F.*, each of these three methods giving essentially identical results within the limits of experimental error. The freezing points of amalgams containing from 16 to 45 atomic % of thallium were found to give a curve indicating conclusively the existence of the solid compound Tl_2Hg_5. The single potential of pure electrolytic thallium was found to be about 2·5 m.v. more negative than that of saturated thallium at the ordinary temperature. J. F. S.

Nitrous-Nitric Complexes of Thallium. L. ROLLA and G. BELLADEN (*Gazzetta*, 1919, **49**, ii, 217—224).—Thallium nitrite,

like barium, strontium, and calcium nitrites (compare Vogel, A., 1903, ii, 591), has a specific electrolytic conductivity below that of the corresponding nitrate, and undergoes normal dissociation. The *E.M.F.* of the cell, thallium amalgam | *N*/10-thallium nitrite | normal electrode, is 0·667 volt at 25°, the same value being obtained if the nitrite is replaced by the nitrate.

Peters found that lead nitrate and nitrite interact in solution, forming well-defined compounds containing both salts. Similarly, thallium nitrite and lead nitrate react, yielding compounds containing Pb, Tl, NO_3, NO_2, and OH. With potassium nitrite and thallium nitrate, however, despite wide variations in the concentrations of the reacting solutions, no product containing potassium could be obtained; the nitrate–nitrites formed, although they have compositions differing greatly from those of Peters' salts, are stable and may be recrystallised unchanged. If the two reacting salts are taken in molecular proportions, the resultant product has the percentage composition Tl 76·65, NO_3 20·58, and NO_2 2·76, whilst in the proportion $TlNO_3$ and $2KNO_2$ the compound obtained has the formula $Tl_3N_3O_8$, the ratio of NO_3 to NO_2 in the complex ion being 2:1. With 3 mols. of potassium nitrite and 1 mol. of thallium nitrate, the product has the percentage composition Tl 82·78, NO_3 6·64, NO_2 5·80, and OH 4·78, and with 4 mols. of the nitrite to 1 mol. of the nitrate the composition is Tl 86·22, NO_3 1·27, NO_2 4·17, and OH 8·34. T. H. P.

Investigations on some Rapid Low Temperature Reactions by means of Heating Curves. J. ARVID HEDVALL and NILS VON ZWEIGBERGK (*Zeitsch. anorg. Chem.*, 1919, **108**, 119—136).—In a previous paper (A., 1919, ii, 26) it was shown that the decomposition of barium peroxide takes place at a much lower temperature in presence of all modifications of silica than when heated alone, a certain amount of barium silicate being formed at the same time. The behaviour of a great number of other oxides when heated with barium peroxide has now been studied by examining the heating curves of the mixtures in molecular proportions. Cuprous oxide reacts violently with barium peroxide at about 130° and is completely oxidised to cupric oxide. The latter decomposes barium peroxide catalytically, the optimum temperature being about 660°. Magnesium and calcium oxides start the decomposition of the peroxide at 250° and 310° respectively, whilst zinc oxide brings about slow decomposition between 200° and 370°, and at the same time forms barium zincate. Purely catalytic action is shown by cadmium oxide, lanthanum oxide, and cerium peroxide, whilst zirconium oxide and stannous and stannic oxide are without action. Alumina acts catalytically and forms an aluminate. Titanium oxide and barium peroxide in molecular proportions, when heated below 300°, evolve oxygen slowly; above 300° a titanate is formed, probably $BaTiO_3$. When the proportions $2BaO_2$ to TiO_2 are used, a basic titanate, completely soluble in acetic acid, is formed. Litharge and barium peroxide between 300° and 400°

give no oxygen, but form a brown product, the nature of which has not been determined. Above 500°, much oxygen is evolved and a product formed, probably Ba_2PbO_4, which leaves a residue of lead peroxide when treated with nitric acid. Vanadium pentoxide reacts vigorously with barium peroxide. When equimolecular proportions are used, reaction begins at 215° and is ended at 530° barium metavanadate, $Ba(VO_3)_2$, being formed. With $2BaO_2$, the metavanadate is first formed, but at 375° a second, very vigorous reaction starts, and the colour changes from brown to white, the product formed being apparently $Ba_2V_2O_7$. Tantalum pentoxide also reacts vigorously, with formation of a tantalate. When arsenic trioxide is heated with barium peroxide (3 mols.), arsenic pentoxide is first formed at 310° to 410°, and above 465° evolution of oxygen begins and barium arsenate is formed. Antimony trioxide behaves differently, as at 200° oxygen is evolved with almost explosive violence. Bismuth trioxide starts a gradual evolution of oxygen at about 250°, and higher oxides of bismuth, or compounds of these with barium oxide, appear to be formed. Chromium sesquioxide is rapidly oxidised above about 225° without evolution of oxygen, barium chromate being formed. The oxides MoO_3, WO_3, U_3O_8, and UO_3 all cause evolution of oxygen and form molybdates, tungstates, and uranates respectively. The lower oxides of manganese are all oxidised, barium manganate being formed. Ferric oxide acts catalytically, and at the same time ferrate is formed. Nickel and cobalt oxides both act catalytically, and are at the same time changed into higher oxides, which, however, do not agree in their properties with the known peroxides of these metals. E. H. R.

Basic Exchange in Permutite. V. ROTHMUND and G. KORNFELD (*Zeitsch. anorg. Chem.*, 1919, **108**, 215—225).—In a previous paper (A., 1918, ii, 315), basic exchange between univalent metals in permutite was studied. The inquiry has now been extended to bivalent metals, with the study of the exchange between copper permutite and the nitrates of magnesium, calcium, strontium, and barium, and it has been confirmed that, with equivalent ions, the reaction is independent of the dilution. The tendency to permutite formation is least with magnesium, and increases steadily from calcium to barium. For the equilibrium between uni- and bi-valent ions, the equation takes the form $(c_1')^2/c_2' \cdot (c_2/c_1^2)^\beta = K$, and this formula has been verified for the exchange between silver permutite and barium nitrate, and for that between calcium and sodium in sodium and calcium permutites. In the latter case a gap was found in the series, showing that calcium and sodium permutites are not completely miscible. The equilibrium for these cases is not independent of the dilution. A few experiments on the exchange between lanthanum and silver permutites showed that in this case the dilution has a marked influence on the equilibrium. E. H. R.

Preparation of Colloidal Mercury by Cathodic Disintegration. A. GUTBIER and G. L. WEISE (*Kolloid Zeitsch.*, 1919, **25**, 97—100).—Colloidal solutions of mercury may be prepared by

striking an arc between a clean mercury surface and a thin platinum foil cathode under water. The most suitable current to employ for the purpose is 3—4 amperes at either 110 or 220 volts. By this means, at ordinary temperatures, the sols are obtained, which have a grey colour, and change from light grey to bluish-grey and then to grey as the concentration increases. The sols are not very stable; on keeping, they coagulate in about twenty-four hours, and are coagulated by very small quantities of electrolytes. In all cases, the coagulation is irreversible. Much more stable sols are produced when a protecting colloid is present; thus, using 1:10 or 1:50 gum arabic solution in water, grey sols are produced, which may be preserved for ten to fourteen days. These sols are also very sensitive to electrolytes and are irreversibly coagulated by the addition of alcohol. J. F. S.

Scandium. R. J. Meyer and B. Schweig (*Zeitsch. anorg. Chem.*, 1919, **108**, 303—317).—It was shown in a previous paper (A., 1914, ii, 369) that the atomic weight of scandium given in the International tables cannot be accepted as a final figure. The impurities likely to be present in scandium preparations separated by the usual methods from the other rare earths are traces of thorium and of the elements of the yttrium earths. It has now been found that complete separation of scandium from these impurities can be effected by fractional crystallisation of scandium formate or of ammonium scandium fluoride, $(NH_4)_3ScF_6$. A sample of scandium oxide, the spectrum of which showed no trace of yttrium lines and only faint traces of those of thorium and ytterbium, was fractionated by the formate method, and when the most soluble fraction was examined spectroscopically, the lines of all these elements showed up very strongly, showing that the spectroscopic test for them is not so sensitive as is usually supposed. The least soluble fraction appeared to be pure scandium formate, and the atomic weight of the metal, determined by the sulphate method, was 45·33 to 45·35. Ammonium scandium fluoride was crystallised from hot, weakly ammoniacal aqueous solution. The impurities separated first from the hot solution, and after these had been filtered off, the solution was allowed to cool. After two or three such crystallisations, the spectrum of the double salt showed no signs of the presence of foreign elements. Atomic weight determinations on the pure materials thus prepared were made by Hönigschmidt by analysis of scandium bromide, the mean result of a series of experiments pointing to 45·1 as the true atomic weight of scandium (A., 1919, ii, 285—286). This is one whole unit above the accepted value. The present authors confirm Hönigschmidt's conclusion that an exact determination of the atomic weight cannot be made by the sulphate method, on account of the impossibility of preparing a pure scandium sulphate free from both basic and acid salts. E. H. R.

The Changes Undergone by certain Alloys of Aluminium. Léon Guillet (*Compt. rend.*, 1919, **169**, 1042—1043).—It has

been shown previously (A., 1902, ii, 264) that certain alloys of aluminium with either iron, manganese, or nickel rapidly crumble to powder in the air. These experiments have been repeated, and this time the alloys of aluminium with iron or nickel remained stable. The aluminium-manganese alloy, containing 85·4% of manganese, crumbled very rapidly in the air, but more slowly in oxygen, nitrogen, or hydrogen, without gaining in weight. The change is to an allotropic modification. Similarly, an alloy of aluminium and antimony fell to powder in moist air, but not in dry air, but in this case the change was chemical, oxidation taking place. W. G.

The Ternary System, Aluminium-Copper-Zinc, with Reference to Zinc in Particular. V. JAREŠ (*Int. Zeitsch. Metallog.*, **10**, 1—44; from *Chem. Zentr.*, 1919, iii, 512—514).—The literature of the binary systems Al–Zn, Al–Cu, and Cu–Zn is critically reviewed, in addition to that of the ternary system, with reference to copper. The author has chiefly investigated the portion of the system Al–Zn–CuAl–$CuZn_4$. This can be resolved into four equilibria triangles, to each of which a ternary, non-variant, pseudo-eutectic point belongs, which (except in one doubtful case) lies outside the equilibrium triangle. At 424°, with 68% zinc, 12% copper, and 20% aluminium, reaction is expressed by the scheme: aluminium mixed crystals + fused mass $\rightleftharpoons$ Al_2Zn_3 + $CuAl_2$; at 418°, with 72% zinc, 11·5% copper, 16·5% aluminium, the equation is $CuAl_2$ + fused mass $\rightleftharpoons$ Al_2Zn_3 + CuAl; at 406°, with 79·5% zinc, 9% copper, and 11·5% aluminium, equilibrium occurs as follows: Al_2Zn_3 + $CuZn_4$ $\rightleftharpoons$ fused mass; at 385°, with 94% zinc, 1% copper, 5% aluminium, the reaction is $CuZn_4$ + fused mass $\rightleftharpoons$ Al_2Zn_3 + Zn. mixed crystals; at 590°, with 76% zinc, 23% copper, 11% aluminium, equilibrium occurs thus: δ + fused mass $\rightleftharpoons$ CuAl + $CuZn_4$. Ternary compounds were not observed. The alloys were prepared by melting the requisite amounts of the pure metals in unglazed crucibles in an electric furnace with alloys containing 20, 50, and 70% of copper. The temperatures were measured with platinum-platinum rhodium or with silver-nickel thermo-elements (calibrated by the m. p.'s bismuth 269°, lead 327°, zinc 419° Sb 630·5°). The changes in the solid alloy resulting from the decomposition of the compound Al_2Zn_3 at 256° were not investigated. The microscopic observations were made with sections etched with aqueous sodium hydroxide solution (2%) or alcoholic picric acid (2%).

The mechanical properties of alloys of aluminium, copper, and zinc, rich in the latter, have been investigated; to secure a near approach to the technical alloys, commercial zinc containing about 1% of lead was used. The hardness of slowly cooled specimens in the system Zn–Al increases rapidly with the aluminium content to about 70 at 10% Al, remains constant to about 20% Al, and then increases very slowly; it reaches a maximum in the system Zn–Cu at about 5% Cu, sinks to a minimum at 12—14% Cu, and subsequently increases very rapidly. The minimum of the Zn–Cu alloy

is also observed in the ternary system Al–Cu–Zn in slowly cooled specimens, but is absent from quickly cooled specimens; the hardness increases considerably more uniformly. The tenacity of Cu–Zn alloys shows a maximum at about 10% Cu, whilst that of Zn–Al alloys increases fairly rapidly with addition of copper to about 8—10% Cu, and then sinks. Fractured surfaces of zinc become finer by addition of aluminium without altering the usual structure; addition of copper causes little alteration in the region of the zinc mixed crystals, but subsequently the fracture is more finely granular. The compressibility of alloys of zinc 90%, Cu 6%, and Al 4% has also been investigated. The tenacity and hardness of brass or ordinary bronze is readily attained in Al–Cu–Zn alloys, but the brittleness of the latter make them an imperfect substitute for the former.

The technical possibilities of Al–Cu–Zn alloys rich in the latter are discussed. The maximum useful copper content is estimated at about 10%, the minimum at about 4%. Aluminium should not exceed 5%, and should be diminished with increasing amounts of copper. The alloys are not suitable for steam; they oxidise too readily, only withstand moderate pressure, and are corroded by many salt solutions, alkalis, and natural waters. They can only be used with caution in making parts subject to considerable mechanical strain. They are frequently useful for fine mechanical work, such as physical instruments. H. W.

The Ternary Systems, $MgO-Al_2O_3-SiO_2$ and $CaO-Al_2O_3-MgO$. A. Meissner (*Zement*, **8**, 296—298, 308—310; from *Chem. Zentr.*, 1919, iii, 511).—The temperature-concentration relationships in the first system of the different crystalline phases in equilibrium with the liquid phases have been investigated, and the results are expressed in diagrams and by a model. A ternary *compound*, $2MgO,Al_2O_3,SiO_2$, unstable at its m. p. and showing considerable tendency to the formation of mixed crystals, has been observed in two forms; the unstable, μ-variety crystallises from glasses at a temperature of about 950°, and passes at a somewhat higher temperature into the stable α-variety. The properties of both forms, more particularly of the α-form, are similar to those of the mineral cordierite. The system $CaO-Al_2O_3-MgO$ is comparatively simple, since it does not yield a ternary compound which is stable in the presence of the liquid phase. Its investigation, therefore, is concerned with the equilibrium of the components CaO, Al_2O_3, and MgO, and of their binary compounds, $3CaO,Al_2O_3$, $5CaO,3Al_2O_3$, CaO,Al_2O_3, $3CaO,5Al_2O_3$, MgO,Al_2O_3, in ternary solution. The results are expressed in a series of temperature–concentration diagrams. A new form of aluminium oxide is designated β-Al_2O_3. The relationship of each of the forms in the binary system $MgO-Al_2O_3$ demands the presence of solid solutions, the amount of which has been estimated. H. W.

Manganese-Bismuth, Manganese-Zinc, and Manganese-Silver Alloys. Paul Siebe (*Zeitsch. anorg. Chem.*, 1919, **108**, 161—183).—The condition diagram for manganese-bismuth alloys

has been determined by the cooling curve method. The two metals are not completely miscible. When more than 23% of manganese is present, two layers are formed, the upper consisting of practically pure manganese, whilst the lower is a 23% solution of manganese in bismuth. Five arrest points were found, corresponding with five crystalline phases. The eutectic horizontal is at 259°, and the other four horizontals, corresponding with the arrest points, are at 442°, 597°, 1043°, and 1252°. The last represents a eutectic containing at most 0·5% bismuth, which lowers the melting point of manganese 13°. From alloys containing up to 0·5% of manganese, pure bismuth first separates; with 0·5 to 9% of manganese, the first compound separates; from 9% to 11% a second compound, and from 11% to 20% a third. The nature of the compounds has not been determined. Between 23% and 99·5% of manganese there is a complete gap. The microscopic appearance of the different crystalline phases is described. The hardness of the alloys increases with the manganese content. They are ferromagnetic, and this property has been shown to be peculiar to the first compound, crystallising from alloys containing between 0·5% and 9% of manganese.

Alloys of zinc and manganese could be prepared containing only up to 50% of manganese. Those containing from 0% to 11% of manganese show an arrest point at 416°, the eutectic point. The eutectic compound contains a very small, undetermined quantity of manganese, which lowers the melting point of zinc 3°. The mixed crystal constituent of the eutectic contains 11% of manganese, and a series of mixed crystals are formed containing up to 50% of manganese. The alloys are brittle and increase in hardness as the manganese content increases.

The behaviour of a series of manganese–silver alloys with a number of chemical reagents has been studied. A sharp distinction was found between those containing 0·22 and 0·24 mol. of manganese and those containing 0·26 and 0·28 mol. respectively. The latter pair were readily attacked by silver sulphate solution, with deposition of silver; by copper acetate and copper sulphate, with deposition of copper; and by sulphuric and hydrochloric acids, with liberation of hydrogen, whilst the former pair, containing less manganese, were unattacked. There was found a similar sharp difference when the electric potentials of the two pairs were compared. Those alloys containing more than 0·25 mol. of manganese appear to behave, both chemically and electrically, practically as pure manganese.

E. H. R.

Fluoro-salts of Tervalent Manganese. I. Bellucci (*Gazzetta* 1919, **49**, ii, 180—186).—The author has isolated the tervalent manganese *fluoro-salt* which causes the anomalous results obtained when Lunge's method of estimating nitrous acid by means of permanganate is applied to solutions containing fluorine ions in high concentration (compare A., 1919, ii, 476). This salt, K_2MnF_5,H_2O, which belongs to the only known type of fluo-salts of tervalent manganese, may be obtained by the action of nitrous acid in

presence of hydrofluoric acid either on potassium permanganate or on a manganous salt, the nitrous acid acting in the former case as a reducing agent and in the latter as an oxidising agent.

T. H. P.

The Atomic Weight of Iron. ALOIS BILECKI (*Zeitsch. anorg. Chem.*, 1919, **108**, 318—320).—In a previous paper, the atomic weights of silver and oxygen were compared through that of manganese (this vol., ii, 26). A similar comparison can be made through the atomic weight of iron. Baxter, by analysis of ferrous bromide, found Fe = 55·8378 when Ag = 107·88, or Fe = 55·90 when Ag = 108·00. By analysis of ferric oxide, Richards and Baxter obtained in two series of experiments 55·90 and 55·883, taking O = 16. A careful comparison of the data of the individual experiments establishes the fact that the ratio of silver to oxygen must be 108 : 16 or 107·88 : 15·9822, thus confirming the conclusion which was arrived at from a consideration of the atomic weight of manganese.

E. H. R.

The Penetration of Iron by Hydrogen. T. S. FULLER (*Trans. Amer. Electrochem. Soc.*, **36**, 16 pp.).—Penetration of iron by molecular hydrogen begins at 325° and increases rapidly with the temperature, but nascent or atomic hydrogen penetrates iron at the ordinary temperature, as shown by these experiments. An iron tube with 1/16-in. walls, connected at the ton to a U-tube device for measuring the volume of gas entering the tube through its walls, was immersed in a 1% solution of sulphuric acid. Hydrogen generated on the outside of the tube passed through the walls, the rate varying with the conditions. The rate was greater for a unit immersed without electrical connections than when the unit was used as a cathode, but in the latter case the greater the current the greater is the penetration. The rate also increases with temperature. Copper is not penetrated by nascent hydrogen, but a coating of tin on the iron increases the rate. Results are given for other conditions and electrolytes. It was proved that there was no penetration by acid, but by gas aloue.

CHEMICAL ABSTRACTS.

Tin Hydride. I. FRITZ PANETH and KARL FÜRTH (*Ber.*, 1919, **52**, [*B*], 2020—2029).—The authors have applied the method which was successfully used in the study of bismuth hydride (Paneth and Winternitz, A., 1919, *ii*, 68) to the problem of the isolation of a hydride of tin. An alloy of tin and magnesium, corresponding with the formula Mg_2Sn, is dissolved in $4N$-hydrochloric or sulphuric acid; the gas which is evolved is filtered through cotton-wool, dried by calcium chloride and phosphoric anhydride, and led through a heated hard-glass tube; a mirror of metallic tin is formed in close proximity to the hot part of the tube, which, when well developed, consists of three zones, a whitish-grey, blackish-grey to black, and finally brown in colour. The reactions of the mirror

are very fully described, the most distinctive of them being the insolubility in cold, concentrated nitric acid, and the formation of purple of Cassius and calomel by gold and mercuric chlorides, respectively, after preliminary treatment of the ring with dry, gaseous hydrogen chloride. Preliminary experiments also show that the gas can be condensed by liquid air and re-evaporated without decomposition, so that its collection in some quantity appears possible. The yields, however, are as poor as in the case of bismuth hydride, only a few thousandths per cent. of the tin of the alloy being converted into the hydride.

[With A. Marschall.]—Preliminary experiment appears to show that lead hydride can exist in the gaseous state. It is formed from the magnesium-lead alloy in yield which is worse than in the cases of bismuth or tin, but better results are obtained by an electrolytic process of reduction. H. W.

The Question of the Existence of Zirconium Monoxide. Robert Schwarz and Hugo Deisler (*Ber.*, 1919, **52**, [*B*], 1896—1903).—Winkler (A., 1890, 1375), Dennis and Spencer (A., 1896, ii, 558), and Wedekind (A., 1905, ii, 596) have studied the reduction of zirconium dioxide by magnesium, and obtained black powders which recombined with oxygen on heating in the air, the increase in weight approximating to that required by the formula ZrO. The experiments have been repeated under various conditions (in a Rose crucible, in a combustion tube in an atmosphere of carbon dioxide, in porcelain tubes at 1000° filled with carbon dioxide or hydrogen or evacuated, and in a crucible fired by thermite), but it is found that it is quite accidental that the black powder left after removing the excess of magnesium and its oxide should increase by the theoretical quantity (nearly 15%) on heating in oxygen. In fact, the more quickly the reduction is performed, the greater is this subsequent absorption of oxygen, rising in one case to 28%.

It appears, therefore, that the black powder is a mixture of metallic zirconium and its dioxide. To test this assumption, various specimens of the powder were heated at about 250° in a stream of chlorine or at high temperatures in hydrogen chloride gas, the sublimate being analysed. It was expected that the free metal would give the tetrachloride, the dioxide remain unattacked, and the monoxide, if any, produce water in the case of hydrogen chloride. No indication whatever could be obtained of the presence of the monoxide. The sublimate consisted of the tetrachloride, and its weight agreed exactly with the increase of weight suffered by the powder when heated in oxygen. The dioxide is not attacked at all, even at 500°. J. C. W.

Zirconyl Compounds with the Oxy-halogen Acids. F. P. Venable and I. W. Smithey (*J. Amer. Chem. Soc.*, 1919, **41**, 1722—1727).—Zirconium hydroxide does not dissolve in iodic acid, and therefore zirconium iodate was prepared by adding iodic acid solution to a solution of zirconyl chloride, when a white precipitate,

insoluble in water, alcohol, and ether, was obtained. It was decomposed by hydrochloric acid, with evolution of chlorine, and at 125° iodine was evolved. The precipitate was filtered without any washing, and other samples were filtered and washed with measured volumes of water with the object of determining the amount of hydrolysis. The unwashed precipitate had the composition $ZrO(OH)_2,2ZrO(IO_3)_2$ when obtained from concentrated solutions, but from dilute solutions the salt is more basic and has the composition $5ZrO(OH)_2,8ZrO(IO_3)_2$. When the second compound was washed with 6 litres of water at the ordinary temperature, the compound had the composition $3ZrO(OH)_2,4ZrO(IO_3)_2$. On washing with 20 litres of boiling water, the compound

$$2ZrO(OH)_2,ZrO(IO_3)_2$$

was obtained, and with 30 litres of boiling water the compound $3ZrO(OH)_2,ZrO(IO_3)_2$ was produced. Zirconium hydroxide is readily soluble in 30% perchloric acid. When the action was allowed to take place at the ordinary temperatures, the compound $ZrO(ClO_4)_2,HClO_4$ crystallised ont in large, triclinic crystals, but when perchloric acid was heated with an excess of zirconium hydroxide, the compound $ZrO(OH)_2,9ZrO(ClO_4)_2$ was obtained in crystal clusters, which were soluble iu alcohol, ether, benzene, chloroform, or carbon tetrachloride, but could not be recrystallised from these solvents. On adding potassium chlorate to a cold concentrated solution of zirconyl perchlorate, crystals of basic zirconyl chlorate, $ZrO(OH)_2,3ZrO(ClO_3)_2$, were obtained. The crystals were extremely deliquescent, very soluble in alcohol, but insoluble in ether. They were faintly yellow in colour, had an odour of chlorine dioxide, and oxidised organic matter very readily.

J. F. S.

Elimination of Vanadium from the Arsenical Waters of the Bellville District, Province of Córdoba, Argentine. Frederico Reichert and Raul Wernicke (*Anal. Soc. Quim. Argentina*, 1919, **7**, 110—113).—Solutions of ferric salts and of ferrous sulphate added in small quantities to alkaline solutions of sodium vanadate cause the precipitation of the vanadium as insoluble ferric vanadate, and also by adsorption on the ferric hydroxide formed. It is proposed to apply the method for the simultaneous removal of arsenic and vanadium from natural waters.

W. S. M.

[Preparation of Potassium Pyroantimonate for the Estimation of Sodium.] J. D. van Leeuwen (*Chem. Weekblad*, 1919, **16**, 1426).—Potassium pyroantimonate, which will remain unaffected for a prolonged period, is made as follows: 20 grams of potassium antimonyl tartrate are mixed with an equal quantity of potassium nitrate, and the mixture is heated to redness in a crucible. When reaction has ceased, the lid is placed on the crucible, and heating continued for fifteen minutes. After cooling, 50 c.c. of warm water are added, and the mass stirred until it

becomes powdery. It is then filtered through a porcelain vacuum filter, the residue is treated with 100 c.c. of cold water, and transferred with the filter paper to a flask containing 500 c.c. of boiling water. After boiling for one minute and rapidly cooling, some aluminium hydroxide is added, the mixture is shaken, and finally passed through an ordinary filter paper. W. J. W.

Bismuth Thiosulphate Compounds. L. VANINO and F. MUSSGNUG (*Arch. Pharm.*, 1919, **257**, 264—266).—The authors have prepared various double thiosulphates of bismuth by making use of bismuth-mannitol solution. Hauser (A., 1903, ii, 487) describes an unstable bismuth sodium thiosulphate, but a stable compound, $BiNa_2(S_2O_3)_3$, which crystallises in small octahedra, is obtainable by the interaction of bismuth-mannitol solution and sodium thiosulphate in presence of manganese chloride. *Bismuth ammonium thiosulphate*, $Bi(NH_4)_3(S_2O_3)_3,2H_2O$, forms a yellow precipitate, which soon changes colour, and on solution in water undergoes decomposition. *Bismuth strontium thiosulphate*,

$Sr_3[Bi(S_2O_3)_3]_2$,

prepared from bismuth-mannitol solution and strontium thiosulphate, forms a yellow, indistinctly crystalline mass, and undergoes hydrolysis when dissolved in water. The bismuth-silver compound, similarly obtained, forms a yellow precipitate, becoming black in a few seconds; the bismuth-copper compound is precipitated only on addition of alcohol.

Unsuccessful attempts were made to prepare bismuth dithionate and trithionate. On addition of sodium trithionate (compare Willstätter, A., 1903, ii, 543) to bismuth-mannitol solution, the liquid soon blackens; as this behaviour is not shown by sodium dithionate, the presence of bivalent sulphur in trithionic acid is proved. T. H. P.

Platotriammine Sulphite. D. STRÖMHOLM (*Zeitsch. anorg. Chem.*, 1919, **108**, 211—214).—When the ammonium salt of trichloroplatosulphonic acid is warmed in aqueous solution with excess of ammonia, *platotriammine sulphite*, $Pt(NH_3)_3SO_3$, is formed as a sparingly soluble, white, microcrystalline powder. It seems to be identical with the substance which was described by Birnbaum (*Annalen*, 1869, **76**, 142) as platotetrammine sulphite. When its hydrochloric acid solution is oxidised with chromic acid, the diammine, $Pt(NH_3)_2Cl_2$, is formed. Solubility determinations showed that only the *trans*-isomeride was formed. This conclusion was confirmed by the preparation of the oxalate, which is quite distinct from that given by the *cis*-compound. E. H. R.

Platinitetrammine Disulphite. D. STRÖMHOLM (*Zeitsch. anorg. Chem.*, 1919, **108**, 184—190).—To determine definitely whether the compound prepared by Cleve by the action of sulphurous acid on Gros's nitrate, $PtCl_2(NH_3)_4(NO_3)_2$, contains bi- or quadri-valent platinum, a study of its formation, reduction,

and oxidation has been made, with the result that the compound has been proved to have the composition $Pt(NH_3)_4(SO_3)_2,2H_2O$. The yield of the disulphite obtained from the nitrate is only about 66% of the theoretical, and a certain amount of sulphuric acid is formed during the reaction, but not so much as would be required to be formed if the platinum were reduced from the quadrivalent to the bivalent condition. When the compound is oxidised by means of chromic acid, the oxygen used is all accounted for by the oxidation of the sulphurous acid to sulphuric acid, that is to say, there is no oxidation of the platinum. The product of the chromic acid oxidation is a *chromi-chromate* of the formula

$$[(OH)_2SO_4Pt_2(NH_3)_8]^{IV}Cr_2O_7,CrO_4.$$

By prolonged heating with dilute sulphuric acid, this compound is transformed into the salt, $[(OH)(SO_4)Pt(NH_3)_4]Cr_2O_7$, previously prepared by Cleve. The same two chromates were prepared from Rajevski's nitrate, $[(OH)ClPt(NH_3)_4](NO_3)_2$.

When the platinitetrammine disulphite is boiled with water or heated with acids, platinotetrammine sulphate is formed, the quadrivalent platinum being reduced by half the sulphurous acid, which becomes oxidised to sulphuric acid, whilst the other half of the sulphurous acid escapes. The same reaction takes place incompletely when the salt itself is heated. E. H. R.

Mineralogical Chemistry.

The Genesis of Petroleum as Revealed by its Nitrogen Constituents. CHARLES F. MABERY (*J. Amer. Chem. Soc.*, 1919, **41**, 1690—1697).—It has already been shown that the heavier varieties of petroleum in the California, Texas, Ohio, Canada, Russian, and similar fields are complex mixtures of the denser hydrocarbons with oxygen, sulphur, and nitrogen derivatives. They all differ widely in composition from the lighter varieties in the eastern territory. An examination of twenty-one specimens of the latter, however, discloses in every case the presence of nitrogen in amount varying from 0·01 to 0·48%, so that the conclusion is justified that nitrogen is contained in the petroleum of all the principal oil fields in forms of combination which could have had their origin only in the remains of vegetable or animal bodies. Presumptive evidence has been shown that the associated hydrocarbons in petroleum had the same origin.

Nitrogen is estimated by Kjeldahl's method on the one hand and by a process which is a combination of the Dumas procedure for nitrogen and the oxygen combustion for carbon on the other. For details of the latter and of the special precautions required in the estimation of such minute proportions of nitrogen in oils, the

original paper must be consulted. The results obtained by the two methods show very fair agreement. H. W.

Probable Identity of Peganite with Variscite. LORENZO MOSCHETTI (*Atti R. Accad. Sci. Torino*, 1917—1918, **53**, 652—656).—The author has analysed and examined physically Breithaupt's peganite (*J. Chem. Physik*, 1830, **60**, 308), his results indicating the identity of this mineral with variscite. The composition given by Hermann (*J. pr. Chem.*, 1844, **33**, 287) for peganite is erroneous. T. H. P.

Identity of Spangite with Phillipsite. F. ZAMBONINI (*Atti R. Accad. Sci. Torino*, 1917—1918, **53**, 47—54).—The spangite described by Mantovani (private communication, 1872) is found to be devoid of magnesium, and its crystallographic characters show that it is identical with the phillipsite of the leucitites found in the neighbourhood of Rome. T. H. P.

The Minerals of the Valley of Gava in the Voltri Group; a New Variety of Talc. EMILIO REPOSSI (*Atti Soc. Ital. Sci. Nat.*, 1918, **57**, 131—155).—The geology of the region is outlined and a number of minerals described. Crystallography or other features are given of garnet, vesuvianite, diopside, hornblende, chlorite, titanite, apatite, pyrite, magnetite, ilmenite, and calcite. Many of these are coated with a mineral, which seems to be a new variety of talc, and is named *gavite*, after the locality. Its properties are: colour, milk-white, yellow, or green, sometimes the colour of nickel salts; lustre in mass, velvety, on surfaces of individual blades, pearly; structure, thin crusts with mammillary surface, made up of bunches of flakes. Microscopic study shows aggregate polarisation, with the optical properties: elongation, +; extinction, parallel; interference colours, brilliant; *n* 1·544 and 1·582 by immersion method, about, double refraction thus 0·038; in all these properties it is similar to talc. It is infusible before the blowpipe, responds to tests for magnesium and silica, and is somewhat readily soluble in hydrochloric acid. Analysis gave:

SiO_2.	MgO.	Fe_2O_3.	H_2O at 110°.	H_2O above 110°	Total.
59·20	28·57	3·23	1·45	6·61	99·06

The water is expelled in two definite stages, in the amounts stated. Disregarding the water below 110°, the revised percentages correspond with the formula $H_4(Mg,Fe)_4Si_5O_{16}$. Gavite differs from talc in the high content of water and in its solubility in acid.

CHEMICAL ABSTRACTS.

The Oxidation of Lava by Steam. J. B. FERGUSON (*J. Washington Acad. Sci.*, 1919, **9**, 539—546).—It is generally supposed that water vapour in volcanic gases would have an oxidising action on any ferrous iron present in the lava. Fresh Kilauean lava has been shown to contain 9·28% ferrous oxide and 1·92% ferric

oxide, and this fact might be used as an argument against the presence of a preponderance of water vapour in the gases. Very little is known, however, of the action of steam on silicate minerals containing ferrous iron, and a number of experiments are here recorded in which ground Kilauean lava was exposed to the action of water vapour in an atmosphere of nitrogen at 1000°. As a result of the heating, there was found a slight decrease in the ferrous iron content of the rock, but this occurred both in presence and absence of steam, which behaved as an inert gas. The experiments leave no doubt that a considerable amount of ferrous iron, when in silicate combinations, can exist in the presence of water vapour at high temperatures. When a sample of the lava was heated strongly in air for two hours, the ferrous iron content fell to 1·94%, but on again heating in a partial vacuum for four hours at 1100°, it rose again to 3·9%. The bearing of these experiments on the interpretation of results obtained by pumping gases from rocks at high temperatures is emphasised. E. H. R.

Cumberland Falls Meteorite. ARTHUR M. MILLER (*Science*, 1919, **49**, 541—542).—This meteorite was seen at midday on April 9th, 1919, passiug over north-eastern Tennessee in a course N. 30 W., its progress being noted and in some instances timed by telegraph and telephone operators. It reached the earth in south-eastern Kentucky, striking with earthquake violence. At the time of writing, seven pieces, ranging from 360 to 2378 grams, have been found. and their covering of glaze indicates that the splitting off from the main mass occurred at a considerable distance from the ground. Fifty-two pieces. weighing from less than 30 grams up to 1800 grams. have been found that are parts of a mass weighing originally about 14 kilos. A chemical examination by ALFRED PETER shows the mineral to be mainly enstatite. through which is disseminated particles of nickel–iron and iron sulphides. D 3·18.

CHEMICAL ABSTRACTS.

Analytical Chemistry.

The Process of Preparation of Charcoal Sticks for Reduction. NESTOR C. ALEXANDRESCU (*Bull. Soc. chim. Romȃnia*, 1919, **1**, 11—12).—The following process for the preparation of charcoal sticks for the reduction test in qualitative analysis is advocated. Thin wood chips, such as are used in match making, are boiled for two minutes in a 2·5% solution of ammonium phosphate, and then dried at a temperature not exceeding 60°. When it is required to carry out the test, half the stick is burnt, and then the test is carried out in the usual manner on the substance previously mixed with sodium carbonate. W. G.

Titrations with Surface-active Substances as Indicators. Estimations of Acidity with the Homologues of the Fatty Acids Series. WILHELM WINDISCH and WALTHER DIETRICH (*Biochem. Zeitsch.*, 1919, **97**, 135—156).—Adopting Traube and Somogyi's method (A., 1915, ii, 101) of estimating the reaction by means of the alteration in the surface tension brought about by the displacement of the acid or the base of the indicator by the acid or base of the medium, the authors tried the homologues of the salts of the fatty acids series up to undecylic acid as indicators. The acids with C_9—C_{11} have been found to be as sensitive as litmus and neutral-red. Free acids can be estimated in the presence of a primary phosphate by using the above acids as indicators.

S. S. Z.

A Considerable Source of Error in Titrations in the Presence of Phenolphthalein. HAEUSSERMANN (*Süddentsch. Apoth. Zeit.*, 1919, **59**, 361—362; from *Chem. Zentr.*, 1919, iv, 396).—The author directs attention to the errors, caused by the presence of free carbon dioxide in distilled water, which occur in titrations in which phenolphthalein is used as indicator. H. W.

Preparation of Phenolphthalein Solution and Paper without the Use of Alcohol. H. CLAASSEN (*Zentr. Zuckerind.*, **26**, 209; *Arch. Suikerind.*, 1919, **26**, 1588—1590).—When alcohol is unavailable, an indicator solution may be prepared by dissolving 1 gram of phenolphthalein in 12·5 c.c. of *N*-sodium hydroxide, and diluting to 500 c.c. with water. The alkali content of the solution is so small that it can be disregarded in factory work. Where greater accuracy is required, the result can be corrected for the alkalinity of the indicator. Test paper can be prepared by immersing paper first in a solution made by diluting 200 c.c. of the above indicator solution to 1 litre, drying, immersing it in a solution of sulphuric acid of the proper strength to give the desired acidity, and drying again. The results obtained with the paper should be verified from time to time by direct titration.

CHEMICAL ABSTRACTS.

Estimation of Bromine in Mineral Waters and Brines. W. F. BAUGHMAN and W. W. SKINNER (*J. Ind. Eng. Chem.*, 1919, **11**, 954—959).—Chromic acid liberates bromine from bromides quantitatively at the ordinary temperature, and the bromine may be removed by aspiration. Chlorides under the same conditions yield only a trace of chlorine, which probably forms chromyl chloride and remains in solution. When a mixture of chlorides and bromides is treated with the reagent, some chlorobromide is formed, and is removed, together with the bromine, on aspiration. In the method of analysis described, the residue from the mineral water is oxidised with chromic acid, with the addition of hydrogen peroxide, and the liberated halogens absorbed in a solution of sodium sulphite and carbonate. This is evaporated, and the residue

again oxidised with chromic acid, and a current of air aspirated through the apparatus, the absorption vessels of which contain potassium iodide solution. In this second aspiration the quantity of chlorine present is so small that only pure bromine is evolved, and its amount is found by titration of the liberated iodine. [See also *J. Soc. Chem. Ind.*, 1920, 19A.] C. A. M.

Test Paper for the Detection of Iodine. ANONYMOUS (*J. Pharm. Belg.*, 1919; from *Ann. Chim. anal.*, 1919, [ii], 1, 357).—One gram of starch is mixed with 10 c.c. of water, 40 c.c. of boiling water are added, the mixture is boiled for two minutes, and 0·5 gram of sodium nitrite is then added. The paste obtained is painted on strips of paper by means of a brush, and the strips are dried. To make the test, a few drops of the solution under examination are poured on the paper, followed by one drop of dilute sulphuric acid. A blue coloration is obtained if the solution contains iodide. The test paper keeps well. W. P. S.

The Spectrocomparator, an Apparatus for the Estimation of the Percentage Saturation of Blood with Oxygen or Carbon Monoxide. AUGUST KROGH (*J. Physiol.*, 1919, **52**, 281—287; from *Chem. Zentr.*, 1919, iv, 210—211).—A modification of Hartridge's method (A., 1912, ii, 488) is proposed which gives satisfactory results and only requires small amounts of blood. The apparatus is fully described and figured in the original, which must be consulted for details. H. W.

Method for bringing Elementary Sulphur into Solution for Analysis. A. P. BJERREGAARD (*J. Ind. Eng. Chem.*, 1919, **11**, 1055).—The finely divided sulphur is dissolved in a small quantity of dry bromine, nitric acid is added, and the mixture heated. The oxidation requires a few minutes only; after the excess of bromine has been expelled, the mixture is diluted with water, boiled with the addition of hydrochloric acid to expel nitric acid, and the sulphuric acid is then precipitated in the usual way as barium sulphate. W. P. S.

Non-protein Sulphur of the Blood. M. KAHN (*Proc. Soc. Exp. Biol. Med.*, 1919, **16**, 139; from *Physiol. Abstr.*, 1919, **4**, 374).—A method of fractionating and estimating the non-protein sulphur of the blood is described. J. C. D.

The Titration of Sodium Thiosulphate Solutions. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 644—657).—The preparation, testing, and application of various substances for the standardisation of thiosulphate solutions are described in detail, and their relative merits for the purpose discussed. The purest forms of potassium dichromate obtainable commercially contain free chromic acid or potassium chromate. A method for the detection and estimation of these is given which depends on the location of a discontinuity in the conductivity curve on the addition of alkali or acid.

If chromic acid is present the addition of standard alkali causes no increase in the conductivity of a dichromate solution until the free acid is neutralised. Similarly, no increase in conductivity is observed on the addition of acid to a solution containing chromate until all the latter has been converted into dichromate. For analytical purposes it is recommended to melt the pure dichromate in an electric furnace before use. The other substances examined are iodine, oxalic acid, cyanogen iodide, potassium iodate, and potassium bromate. All these are easily purified, and give results in the titration of thiosulphate with an error of less than 0·1%. The greatest error, 0·07%, was observed in titrating with dichromate.

W. S. M.

Influence of the Position of Substituents on the Behaviour of Aromatic Nitro-compounds in the Kjeldahl Estimation of Nitrogen. B. M. MARGOSCHES and ERWIN VOGEL (*Ber.*, 1919, **52**, [*B*], 1992—1998).—The behaviour of the isomeric nitrophenols, nitrobenzoic acids, and nitrobenzaldehydes when treated with sulphuric acid and potassium sulphate has been investigated; it is found that the nitrogen content of the ortho-derivatives can be correctly estimated in this manner, but that the results for the meta- and para-derivatives are much too low. The favourable action of the hydroxy- or alkyloxy-group in the ortho-position to the nitro-group is further shown by the fact that the process gives exact results with 2-nitroresorcinol, 3-nitro-*p*-cresol, and *o*-nitrophenetole, but low results with *p*-nitrophenetole. A further series of experiments shows that the presence of *o*-nitrophenol or of *o*-nitrobenzoic acid has a favourable influence on the behaviour of the corresponding meta- and para-derivatives, and that this action cannot be ascribed solely to their content of phenol or benzoic acid. The possibility that condensation products of the *o*-nitro-compounds may be the active agents has led to an investigation of the behaviour of phthalic acid, phthalic anhydride, and phenolphthalein under like conditions, but the expected favourable action was not observed. The use of salicylic acid appears particularly advantageous in the case of meta-compounds. It is somewhat remarkable that the three isomeric nitrocinnamic acids yield accurate results.

A further series of determinations is recorded with 2 : 4-dinitrophenol, 2 : 4-dinitro-α-naphthol, 2 : 4-dinitrobenzoic acid, 2 : 4-dinitrotoluene, 3 : 5-dinitrobenzoic acid, 2 : 6-dinitrotoluene, and 2 : 4 : 6-trinitrophenol; the results are considerably too low in every case, although concordant among themselves. The facts, however, that the 2 : 4-dinitro-compounds give higher values than the corresponding 3 : 5- or 2 : 6-dinitro-derivatives, and that 2 : 4-dinitrophenol gives results almost identical with those obtained with 2 : 4-dinitrotoluene, are in accordance with the observations made with the mononitro-compounds.

H. W.

Grete's Volumetric Method (for Estimating Phosphoric Acid). R. W. TUINZING (*Landw. Versuchs.-stat.*, 1919, **94**, 191—195. Compare A., 1916, ii, 490).—This method was found

to be trustworthy. Directions are given for the preparation of the ammonium molybdate–gelatin solution used, and for the recovery of ammonium molybdate from the residual solutions. W. P. S.

Behaviour of certain Organic Arsenic Compounds in Marsh's Test. DOMENICO GANASSINI (*Boll. Chim. Farm.*, 1919, **58**, 385—390).—The addition of platinum chloride to promote the evolution of hydrogen is inadvisable, even in the case of mineral arsenic, since it may fix part of the arsenic as platinum arsenide. In the case of cacodylic acid, platinum chloride in large excess combines to form a double compound, cacodylplatinochloride, which may remain undecomposed. An analogous compound is formed between platinum chloride and methylarsinic acid. Cacodylic acid, in Marsh's test, produces an orange-yellow deposit in addition to the ordinary black deposit. This probably consists of erythrarsine. By heating the hydrogen flask to about 335° in a bath of melted lead only the orange-yellow deposit is obtained. Methylarsinic acid and neosalvarsan under the same conditions also yield yellow deposits, but these may be distinguished from the cacodylic acid deposit by the fact that during the formation of the former the gas does not form dense, white fumes. The gas from the methylarsinic acid test gives a yellow precipitate with Bettendorf's reagent (stannous chloride solution saturated with hydrogen chloride), whilst the lemon-yellow ring from neosalvarsan is only formed at a high temperature, does not change to black, and is readily soluble in ammonia solution. Atoxyl and salvarsan yield only the ordinary black rings in the test. [See also *J. Soc. Chem. Ind.*, 1920, 42A.] C. A. M.

Separations in the Arsenic Group. WILHELM STRECKER and ADOLF RIEDEMANN (*Ber.*, 1919, **52**, [*B*], 1935—1947).—The authors recommend the following modification of the distillation method for the estimation of arsenic. The arsenic solution is placed in a flask provided with a dropping funnel and connected through an efficient worm condenser with a vessel containing water; the flask is half filled with concentrated hydrochloric acid, potassium bromide (1·5 grams), and a few pieces of porous earthenware are added. The contents of the flask are heated to gentle boiling, and thionyl chloride (10 c.c.) is gradually run in at such a rate that the time of addition is half an hour. The distillate is diluted with water to 700—800 c.c., boiled under reflux in a brisk current of carbon dioxide until sulphur dioxide is completely expelled, and the sulphur has collected (this should be the case in half an hour at the most), and filtered. Arsenic is estimated in the filtrate as the trisulphide. Phosphorus trichloride (25 c.c.) may replace the thionyl chloride, in which case the subsequent boiling of the distillate is unnecessary; on the other hand, the presence of phosphorous acid in the residue often causes complications in subsequent estimations. The method gives accurate results, and can be applied to the separation of arsenic from antimony, tin, copper, lead, mercury

and iron, and for the estimation of arsenic and iron in arsenide of iron.

The separation of antimony from tin can be effected by taking advantage of the fact that antimony chloride is volatile at 155—165° from solutions in which the tin can be rendered non-volatile by the presence of phosphoric acid; the tin can be volatilised subsequently at a somewhat higher temperature by taking advantage of the fact that the addition of hydrobromic acid destroys the restraining action of the phosphoric acid. The authors have attempted to shorten the time required for this separation by utilising the catalysing action of hydrobromic acid from the commencement, but the results are unsatisfactory, since tin distils over with the antimony, the catalysing influence of hydrogen bromide outbalancing the restraining effect of phosphoric acid. On the other hand, the use of hydrobromic acid is very advantageous in the separation of antimony or tin alone from other elements, and does not require the absence of nitric acid. Thus, in the separation of antimony and copper, the hydrochloric acid solution of the metals is added to concentrated sulphuric acid (6 c.c.) and phosphoric acid (D 1·78, 7 c.c.) contained in a distillation flask connected with a receiver containing hydrochloric acid. The contents of the flask are heated at 160°, and a mixture of concentrated hydrochloric acid (10 volumes) and hydrobromic acid (D 1·78, 1 volume) is added at such a rate that the temperature remains constant. The antimony is completely removed in thirty minutes. The separation of antimony from lead is accomplished similarly.

Tin is quantitatively separated from copper and lead in an analogous manner; the solution of the metals in concentrated hydrochloric acid is treated with sulphuric acid (12 c.c.) and distilled at 160° with the regulated addition of the hydrochloric–hydrobromic acid mixture (20 c.c.). The process is complete in half an hour; the tin is precipitated from the distillate as the sulphide and weighed as the oxide. The method can be applied to the estimation of tin n brass.

The separation of antimony and tin from mercury cannot be ffected in this manner, since the latter is also partly volatilised.

A novel type of filter tube is described which is constructed by rawing out the end of a piece of wide glass tubing so as to form stem; a filter disc covered with asbestos rests on the shoulder of he wider tube, which is further provided with a ground-in cap in hich a capillary opening is made. H. W.

Early Developments in Organic Macro- and Micro-analysis. . V. Dubský (*Chem. Weekblad*, 1919, **16**, 1482—1493).—The uthor gives a retrospect of the work of various experimenters in onnexion with the analysis of organic substances, and indicates the nes along which research progressed. W. J. W.

Gas Analytical Combustion with Copper Oxide. E. Ott . *Gasbeleucht.*, 1919, **62**, 89—90; from *Chem. Zentr.*, 1919, 171—172).—Uncertainties in fractional combustion with copper

oxide arise in consequence of the dissociation, $CuO = Cu + O$, which can be eliminated by subsequent, repeated passage of the nitrogen over the material in the quartz tube, which is maintained at a low red heat. Preparation of chemically pure nitrogen by means of phosphorus and heated copper oxide is liable to error, and recourse should be had to the pyrogallol method. Copper oxide does not appear to be suitable for gas analyses in which the carbon dioxide formed by combustion is measured. H. W.

Estimation of Carbon Monoxide in Blood. D. D. Van Slyke and H. A. Salvesen (*Proc. Soc. Exp. Biol. Med.*, 1919, **16**, 140; from *Physiol. Abstr.*, 1919, **4**, 374).—The blood is treated as in the estimation of oxygen by Van Slyke's method. A mixture of carbon monoxide and oxygen with a slight amount of nitrogen is obtained. The oxygen is absorbed by alkaline pyrogallol solution. The residual gas, after a correction has been made for nitrogen, is carbon monoxide. J. C. D.

A Micro-method for the Estimation of Calcium in Blood-serum, and other Organic Substances. D. J. de Waard (*Biochem. Zeitsch.*, 1919, **97**, 176—186).—The substances are evaporated and incinerated, and the salts of the ash extracted with dilute hydrochloric acid. The calcium is precipitated from the solution as the oxalate, which is centrifuged, washed, dissolved in dilute acid, and titrated with potassium permanganate. 0·1 Mg. of calcium can be estimated by this method with an error of 4%. S. S. Z.

A Direct Micro-estimation of Calcium in the Serum. D. J. de Waard (*Biochem. Zeitsch.*, 1919, **97**, 186—189).—All the calcium can be precipitated directly from the serum by means of ammonium oxalate and be estimated by the method described in the preceding abstract. The difference between an estimation carried out on the incinerated serum and on the original serum was only 0·001 mg. of calcium per c.c. S. S. Z.

Ferrous Sulphide as an Indicator in Acidimetry and a New Volumetric Method for the Estimation of Zinc. J. Houben (*Ber.*, 1919, **52**, [*B*], 1613—1621).—Since the production of ferrous sulphide is prevented by the slightest traces of acids, it is possible to titrate an acid by adding a crystal of pure ferrous ammonium sulphate, passing in well-washed hydrogen sulphide (not enough to saturate the solution), and running in alkali until the black colour of ferrous sulphide is permanent. Experiments with hydrochloric and sulphuric acids on the one hand and alkali hydroxides and carbonates or borax on the other show that the end-point is quite as definite as it is in the case of methyl-orange or phenolphthalein. The only indistinct end-point is found when titrating sulphuric acid with borax, but here the difficulty may be overcome by running in more acid until the black colour just disappears again. The method is obviously useful in the case of coloured liquids, or when working in a bad light.

In the case of zinc salts, hydrogen sulphide completely precipitates zinc as sulphide from the sulphate if the solution is less than 0·2*N*, and from the chloride if the concentration is below 0·067*N*. A titration of the free acid produced would therefore be a means of estimating zinc in its neutral salts, and here the above use of a ferrous salt proves its worth. The solution is saturated with hydrogen sulphide, some ferrous ammonium sulphate is added, and alkali is run in, preferably borax solution, until the white turbidity becomes brown. A "back titration" with an acid is not possible in this case, however, without first filtering the zinc sulphide, as a double zinc-ferrous sulphide is formed which is not quickly broken up. Of course, cobalt and nickel salts must be absent.

Examples of the application of the method to metallic zinc, zinc salts, zinc ash, and blende show that the results approach those obtained by gravimetric analysis very closely, in fact much more so than those given by any other volumetric method. Blende is examined as follows. About 5 grams of the mineral are digested with 40 c.c. of concentrated hydrochloric acid and 40 c.c. of water, the solution filtered and saturated with hydrogen sulphide, filtered again, and diluted to 1000 c.c. with dilute hydrochloric acid. Portions of 50 c.c. are now neutralised with sodium carbonate, using methyl-orange, treated with hydrogen sulphide for half an hour, mixed with ferrous ammonium sulphate, and titrated with borax or sodium carbonate.

The alkalimetric titration of ferric salts may be carried out by employing the same principles. J. C. W.

Electrometric Analysis with Potassium Ferrocyanide. ERICH MÜLLER (*Zeitsch. angew. Chem.*, 1919, **32**, 351—352).—Electrometric titration of lead and zinc salts with potassium ferrocyanide solution is trustworthy, but the method fails in the case of other metals owing to the fact that the precipitates produced do not have definite compositions. W. P. S.

Colorimetric Estimation of Lead Dioxide in Litharge. WALLER V. MORGAN (*J. Ind. Eng. Chem.*, 1919, **11**, 1055).—The method depends on the fact that lead dioxide oxidises aniline to aniline-purple, and that the coloration obtained is proportional to the amount of the dioxide present. Five grams of the litharge containing lead dioxide are boiled for one minute with 2 grams of aniline hydrochloride dissolved in 10 c.c. of water and 5 c.c. of concentrated hydrochloric acid; the mixture is then filtered and the coloration exhibited by the filtrate compared with those given under the same conditions by litharge containing known amounts of lead peroxide. W. P. S.

Complex Internal Salts in Quantitative Analysis. I. I. BELLUCCI and A. CHIUCINI (*Gazzetta*, 1919, **49**, ii, 187—216).—The authors summarise and criticise published work on the applications of α-nitroso-β-naphthol and "cupferron" to the separation and estimation of metals.

For the separation of copper, neither of these reagents offers appreciable advantages over ordinary analytical methods, except perhaps for the separation of copper from arsenic and, more particularly, from antimony. For the separation of iron, cupferron is to be preferred to α-nitroso-β-naphthol, chiefly because the ferric precipitate obtained with the former withstands a greater degree of free mineral acidity, and is therefore more easily freed from extraneous metals, and also because the precipitate is less voluminous. α-Nitroso-β-naphthol serves principally as a reagent for cobalt, and also as a reagent for palladium, whilst cupferron acts as a reagent for titanium, zirconium, and vanadium, as well as for iron. The two compounds assume, indeed, the character of general reagents for groups of elements which contain, however, elements quite different from those usually classed together. T. H. P.

Detection of Cerium. FR. FEIGL (*Österr. Chem. Zeit.*, [ii], **22**, 124—126; from *Chem. Zentr.*, 1919, iv, 592).—Lecoq's reaction is much more distinctly obtained after the addition of a small quantity of an aluminium salt, but is not applicable in the presence of iron. A vivid blue coloration is obtained when cerium dioxide is moistened with a solution of benzidine in acetic acid; other cerous and ceric compounds, with the exception of cerous fluoride, cerous carbonate, and double sulphates of cerium, behave similarly. The reaction is most sensitive when the solution under investigation is made just alkaline with sodium or potassium hydroxide, heated to boiling, filtered, and the filter paper treated with a drop of benzidine solution; 0·02 mg. of cerium per litre can be thus detected. The other metals which belong to the ammonium sulphide group of the rare earths, with the exception of thallium, do not show the reaction. The absence of other oxidising agents and of manganese, cobalt, thallium, and chromate is essential, since the reaction depends on oxidation. Faintly acid solutions of iron also give the reaction; after previous addition of sodium or potassium hydroxide, a coloration is not observed. In the presence of iron, it is advisable to precipitate cerium as the fluoride and to convert the latter by alkali hydroxide into the hydroxide, since precipitated ferric hydroxide carries down notable amounts of cerium, which are thus removed from the sphere of action. H. W.

Soil Analysis. F. MÜNTER (*Landw. Versuchs.-stat.*, 1919, **94**, 181—189).—For the estimation of iron, aluminium, calcium, magnesium, potassium, and phosphoric acid in a soil, it is recommended that 300 grams of the sample be mixed with 900 c.c. of concentrated hydrochloric acid and shaken occasionally during forty-eight hours; the solution is then decanted, filtered, and 300 c.c. of the filtrate are evaporated with the addition of ammonium chloride. The residue obtained is treated with nitric and hydrochloric acids, again evaporated, this operation is repeated, and the final solution in hydrochloric acid is used, after separation of the silica, for the estimation of the above-mentioned constituents. W. P. S.

Application of Hæmatoxylin to the Detection of Iron in Tissues. J. Mawas (*Compt. rend. Soc. Biol.*, 1919, **82**, 155—158; from *Chem. Zentr.*, 1919, iv, 245).—The author considers that the reaction of hæmatoxylin with ferrous ions is to be ascribed to salt formation, and not, as Macallum assumed, to oxidation. The latter's statement that the reaction only occurs with inorganic iron is incorrect, since iron compounds of the albumins, which are not acted on by hydrogen sulphide or ammonium sulphide, but are affected by potassium ferro- or ferri-cyanide, also show this change. The formation of Prussian-blue is a more delicate test for the presence of iron in tissues; nevertheless, the author has obtained useful results with hæmatoxylin, particularly in certain cases of disease of the eye. The affinity of the hæmatoxylin for the chromatin of the nucleus, whereby a similar coloration is developed, is disadvantageous.
H. W.

Brazilin and its Iron Lakes. J. Mawas (*Compt. rend. Soc. Biol.*, 1919, **82**, 158—159; from *Chem. Zentr.*, 1919, iv, 245).—Brazilin is a more sensitive and more rapid reagent than hæmatoxylin (preceding abstract); its aqueous solution, pale red with an orange fluorescence, gives dark brown, insoluble lakes with ferrous salts. In aqueous or alcoholic solution, it colours tissue containing iron dark brown within a few minutes, whilst the nucleus becomes reddish-violet. Differentiation which may be necessary owing to over-colouring is effected with alcohol and chloroform, or, preferably, with alcohol containing 1% of hydrogen chloride. The nucleus becomes practically decolorised, whilst the iron pigment is unaffected; the former again becomes reddish-violet when washed with dilute aqueous alkali.
H. W.

Iodometric Estimation of Iron. I. M. Kolthoff (*Pharm. Weekblad*, 1919, **56**, 1565—1568).—The estimation of ferrous iron by means of iodine with addition of a pyrophosphate gives results which are about 3% too low owing to oxidation of the iodine by dissolved oxygen in the solutions. If sulphuric acid and sodium hydrogen carbonate are added to eliminate the oxygen, the error is reduced to 0·8—1%. A more suitable method which gives accurate results is the following: 25 c.c. of 0·1*N*-potassium bromate and 10 c.c. of 25% phosphoric acid are added to 10 c.c. of 0·1*N*-ferrous solution to which a few drops of acid have been added. After remaining for five minutes in a stoppered flask, 5 c.c. of potassium iodide and 2 drops of molybdate solution are added, the iodine being titrated after five minutes with thiosulphate.

The purpose of the phosphoric acid is to combine with the ferric ions and prevent them interacting with the potassium iodide, and the molybdate is added to accelerate the reaction of the bromate and iodide.
W. J. W.

Volumetric Estimation of Iron. J. Houben (*Ber.*, 1919, **52**, [*B*], 2072—2076. Compare this vol., ii, 53).—The process

ermits *the estimation* of ferrous and ferric iron and free mineral cid in a solution.

A portion of the solution is completely reduced by hydrogen sulhide and titrated with *N*-potassium or sodium hydroxide solution ntil the dark coloration due to the incipient precipitation of errous sulphide is observed, which does not disappear after vigorus shaking; the free acid plus one-third of the acid originally comined with the ferric salt is thereby estimated. A second portion f the solution is reduced with sulphur dioxide (air being completely xcluded), most of the excess of the latter is removed by boiling, nd the cooled solution is titrated with *N*-alkali as before, after eing treated with hydrogen sulphide, which completes the removal f sulphur dioxide. The free acid plus two-thirds of the acid originlly united to the ferric iron is thus estimated. The difference etween the two titrations multiplied by three gives the number of c. of *N*-ferric chloride solution originally present. If this number s subtracted from the smaller of the two burette readings, the diference is the number of c.c. of *N*-acid which were uncombined in he solution The ferrous salt is estimated in the usual manner. 'est *analyses show the method to have a high degree of accuracy.*

H. W.

Separation of Iron, Aluminium, Chromium, Glucinum, Titanium, and Zirconium by the Sodium Carbonate Method. '. Wenger and J. Wuhrmann (*Ann. Chim. anal.*, 1919, [ii], **1**, 37—339).—A method described previously by Wenger and Wunder A., 1912, ii, 687) may be applied when the mixture contains itanium or zirconium, but not both. After fusion with sodium arbonate, the *insoluble iron and zirconium oxides may be treated* 'ith hydrochloric acid (1:1), in which the zirconium oxide is isoluble. In the absence of zirconium, iron and titanium may be eparated by one of the known methods, even in the presence of lucinum. [See, further, *J. Soc. Chem. Ind.*, 1920, 46A.]

W. P. S.

A New Method for the Volumetric Estimation of Nickel. osef Hollufa (*Monatsh.*, 1919, **40**, 281—291).—The process epends on the fact that, when a nickel salt reacts with dimethyllyoxime, acid is liberated, which is estimated by titration with lkali in the presence of phenolphthalein or methyl-red.

The standard *N*/50-solution is prepared by dissolving 4·6400 rams of pure dimethylglyoxime in the requisite quantity of 97% lcohol *(300—400 c.c.); 20 c.c. of N*-potassium hydroxide solution re added with constant shaking, and the solution is diluted to 000 c.c. with distilled water free from carbon dioxide and filtered fter twenty-four hours from any slight precipitate of potassium arbonate. (The alcohol used must be free from aldehyde and eutral in reaction.) The alkali content of the solution is checked y titration with standard acid, using phenolphthalein or methyled as *indicator*. The nickel solution under examination is diluted

to the required extent, and exactly neutralised with $N/10$- or $N/50$-potassium hydroxide solution. 2—5 C.c. of the standard solution are added, and, after vigorous agitation, the solution is gently warmed, whereby the precipitate is caused to collect, leaving a clear liquor; the standard solution is then gradually added with frequent agitation until the solution acquires a permanent, pale pink coloration. In consequence of the bulky nature of the nickel precipitate, the amount of the metal in the solution should not exceed 0·03 gram.

The method is particularly advantageous in dealing with very small quantities of nickel, and titration can readily be effected with $N/100$-solutions if methyl-red is substituted for phenolphthalein as indicator. The results are not affected by the presence of the alkali salts of strong acids. Further details are promised in a subsequent communication. H. W.

Iodometric Estimation of the Chromic Acid in Lead Chromate. MAX GRÖGER (*Zeitsch. anorg. Chem.*, 1919, **108**, 267—272).—The iodometric method of estimating chromic acid has not hitherto been used for lead chromate on account of the impossibility of completely decomposing the chromate by means of dilute sulphuric acid. Dilute hydrochloric acid dissolves lead chromate completely, but hydrochloric acid has a reducing action on chromic acid, with liberation of free chlorine, and has therefore not been used to dissolve lead chromate. It is now found, however, that if the hydrochloric acid is sufficiently dilute, its reducing action is negligible. Experiments showed that when acid of 1·25N strength or less was used, in the proportion of 25HCl to 1 mol. of chromate, no reduction took place after boiling the solution for three hours. With stronger hydrochloric acid, the rate of reduction increased rapidly with the concentration of the acid. For carrying out an analysis, about 0·3 gram of lead chromate is dissolved in 50 c.c. of 1·25N-hydrochloric acid by gently heating. The solution is cooled, 1 gram of potassium iodide added, allowed to remain for ten minutes, diluted with 100 c.c. of water, and the free iodine titrated with sodium thiosulphate. There is no need to filter off the precipitated lead iodide, as the colour of this does not interfere with the end-point. After the end of the titration, free iodine again appears after a short time. This is due to atmospheric oxidation of hydriodic acid, a reaction which appears to be catalysed by the lead iodide present. The results obtained by this method are generally about 0·5% too high. E. H. R.

Detection of Molybdenum by means of Xanthic Acid. J. KOPPEL (*Chem. Zeit.*, 1919, **43**, 777—778).—Molybdenum compounds give a characteristic red to plum-coloured reaction with xanthic acid, which was first described by Siewert (*Zeitsch. ges. Naturw.*, 1864, **23**, 5). The test is preferably applied by acidifying the solution with a mineral acid, after the addition of a trace of solid potassium xanthate, and is capable of detecting molybdenum in a solution containing 0·00000064 gram per c.c. The reaction is

weaker when phosphoric, formic, or acetic acid is used for the acidification, and much weaker with salicylic acid, whilst when oxalic, citric, or tartaric acid is used, there is little, if any, coloration. Analogous xanthic compounds are formed by copper, iron, cobalt, nickel, etc., but the colorations do not interfere with the molybdenum test. Vanadic acid forms a yellow compound and uranic acid a brown compound, which, like the molybdenum compound, are soluble in ether and other organic solvents. Tungstic acid, if present in very large preponderance, may interfere with the test. The molybdenum compound may be obtained as a black oil by mixing a solution of 2 grams of ammonium paramolybdate with 1 gram of potassium xanthate. When vigorously stirred, this oil solidifies, forming black crystals with green surface reflections. The mean analyses of Siewert's solid preparation agree with the formula $MoO_3(OEt\cdot C\cdot S\cdot S\cdot H)_2$. [See also *J. Soc. Chem. Ind.*, 1920, January.] C. A. M.

Colour Reactions of Molybdenum and Tungsten. II. G. A. BARBIERI (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 390—392. Compare A., 1919, i, 549).—According to Péchard (A., 1894, ii, 319), replacement of the hydrochloric or sulphuric acid used in Braun's reaction by acetic acid results in the formation of a yellow coloration, and, with concentrated solutions, of a yellow, crystalline precipitate, due to conversion of the molybdate into trimolybdate, and union of this with the thiocyanate present to form an additive compound, for instance, $KCNS,K_2O,3MoO_3,4H_2O$. On repetition of Péchard's reaction with ammonium thiocyanate and ammonium permolybdate or tri- or tetra- or normal molybdate, the author finds that in all cases the *additive* compound,

$$NH_4SCN,(NH_4)_2O,4MoO_3,5H_2O,$$

is formed, and in no case an additive compound of the trimolybdate. From potassium trimolybdate and thiocyanate in presence of acetic acid, the corresponding *compound*, $KSCN,K_2O,4MoO_3,5H_2O$, is formed; both potassium and ammonium compounds form yellow, acicular crystals.

Ammonium tetramolybdate, $(NH_4)_2O,4MoO_3,2\frac{1}{2}H_2O$, may be obtained by the action of acetic acid on ammonium permolybdate in aqueous solution (compare Junius, A., 1905, ii, 825). T. H. P.

Qualitative and Quantitative Test for Molybdenum in Steel and Iron. SIEGFRIED LAURENS MALOWAN (*Zeitsch. anorg. Chem.*, 1919, **108**, 73—80).—A specific and very sensitive test for molybdenum is given by xanthic acid. The test is best carried out with freshly prepared xanthate solution in the following manner. Absolute alcoholic potash is shaken with excess of carbon disulphide until no more of the latter is dissolved. To the solution so obtained, 30% acetic acid is added until it shows a slight yellow turbidity, and the reagent is added drop by drop to the solution to be tested. If molybdenum is present, an intense red colour

develops, which is quite stable in water, and the intensity of which is proportional to the quantity of molybdenum present. The sensitiveness of the reaction is such that 0·000005 gram of molybdenum in 0·0007% solution can be detected with certainty in presence of other elements. The coloured product is readily soluble in ethyl or amyl alcohol, ether, or chloroform, less easily in petroleum and benzene. It is readily extracted from its reddish-violet ethereal solution by alkalis, from which acids precipitate it. The ethereal solution decomposes on keeping, with formation of molybdenum sulphide. The reaction is not given by vanadium, tungsten, titanium, or uranium; chromates give a dark coloration with xanthic acid, and should be reduced, if present, before the test is made. The reaction can be used for the colorimetric estimation of molybdenum, the coloured product being extracted with a mixture of 65% ether and 35% light petroleum, and a mixture of 30% ether and 70% light petroleum used for dilution for comparison with the standard solution. If pure ether is used, decomposition takes place too rapidly for accurate determinations to be made. E. H. R.

Colorimetric Method for the Estimation of Small Quantities of Uranium. Müller (*Chem. Zeit.*, 1919, **43**, 739—740).—The method depends on the red coloration obtained when a uranyl salt is treated with sodium salicylate; the coloration yielded by any uranyl salt solution is compared with that produced by a known amount of uranium under the same conditions. Free mineral acid, acetic acid, iron, alcohol, or acetone must not be present, but neutral alkali salts do not interfere. The method is suitable for the estimation of uranium in solutions containing as little as 0·02% of the metal. W. P. S.

Estimation of Zirconium by the Phosphate Method. G. E. F. Lundell and H. B. Knowles (*J. Amer. Chem. Soc.*, 1919, **41**, 1801—1808).—Zirconium can be quantitatively precipitated as secondary zirconium phosphate in cold or tepid solutions containing from 2% to 20% by weight of sulphuric acid, provided that a ten- to one hundred-fold excess of the precipitant, diammonium hydrogen phosphate, is used. Hydrolysis, which occurs when the phosphate precipitate is washed with water, can be almost entirely avoided by the use of a cold 5% ammonium nitrate solution for washing. Zirconium pyrophosphate, for which the ZrO_2 factor is 0·4632, is obtained on ignition of a secondary zirconium phosphate which has been washed with ammonium nitrate solution. No definite composition can be ascribed to the compound resulting when secondary zirconium phosphate which has been washed with water is ignited. Zirconium can be quantitatively separated as phosphate in a 20% sulphuric acid solution from iron, aluminium, chromium, cerium, and thorium. The separation from titanium can also be effected provided hydrogen peroxide is present. J. F. S.

Gas-analytical Separation of Acetylene, Ethylene, and Benzene. W. D. Treadwell and F. A. Tauber (*Helv. Chim. Acta*, 1919, **2**, 601—607).—The quantitative absorption of acetylene from mixtures containing it, together with ethylene and benzene vapour, is conveniently effected with a solution of mercuric cyanide (20 grams) in 2*N*-sodium hydroxide solution (100 c.c.); the gas is shaken with the mixture (5 c.c.) for one to two minutes, at the end of which the acetylene is completely absorbed, whilst ethylene and benzene vapour are unaffected.

A solution of mercuric nitrate (20 grams) in 2*N*-nitric acid (100 c.c.) which has been saturated with sodium nitrate is recommended for the absorption of ethylene in the presence of benzene vapour; the gas is shaken with 5—10 c.c. of the solution for two to three minutes. Propylene appears to behave similarly to ethylene, since it is indifferent to alkaline mercuric cyanide solution, whilst readily absorbed by mercuric nitrate solution.

H. W.

Dehydrogenation of Hydrocarbons by means of Palladium-black. Jenö Tausz and Nikolaus von Putnoky (*Ber.*, 1919, **52**, [*B*], 1573—1583).—Zelinski has shown that *cyclo*hexanes are converted into benzene hydrocarbons by exposing them to the action of palladium-black at 300°, whereas hexane and *cyclo*pentanes are unchanged (A., 1913, i, 167). This seemed to offer a process whereby *cyclo*hexanes could be estimated in the presence of paraffins, and a method has now been developed which gives satisfactory results within certain limits.

The first difficulty to be overcome was the preparation of a sufficiently active catalyst, for Zelinski's agent is spoilt by mixtures of paraffins and *cyclo*hexane long before the latter is completely dehydrogenated. In the reduction of palladium solutions, it is usual to employ formic acid, any excess being destroyed by the palladium-black itself. It seemed possible, therefore, that the activity of the catalyst would suffer in such a treatment, and as it was found that the activity towards formic acid is parallel to the activity towards *cyclo*hexane, it was decided to use no more than the theoretical quantity of the reducing agent. This has the desired effect, the catalyst being much more active. For example, two specimens of 1 gram each, prepared by Zelinski's method, produced 1·8 and 11·2 c.c. of gas from formic acid, but ten samples made by the new process, which is described in detail, gave on an average 458 c.c., one portion developing as much as 840 c.c.

With such an active catalyst, the quantitative dehydrogenation of *cyclo*hexane in various mixtures with hexane may be easily realised; but then another disturbing factor appears, namely, that at 300° the saturated paraffins themselves are to a certain extent converted into unsaturated hydrocarbons by palladium black. The small amount of hydrogen set free by the paraffins, however, reaches a constant volume after an hour or two, and although a little more gas is liberated when the catalyst is renewed, an equilibrium

digested by itself in the Zeisel apparatus at 120—125°, it does so behave when added to glycerol. In fact, the excess of silver iodide corresponds with the amount of *s*-di-iodopropane produced if the quantity of trimethylene glycol is small. As a consequence, Zeisel's method is not applicable to the estimation of fermentation glycerol (the German "protol"-glycerol), for this contains trimethylene glycol. J. C. W.

Chromatic Reactions of Formaldehyde with certain Aromatic Compounds. ARTURO ROSSI (*Boll. Chim. Farm.*, 1919, **58**, 265—270).—Colorations, which are not necessarily distinctive of the aldehyde, are given by formaldehyde in 0·1 or 0·001% aqueous solution, when added to sulphuric acid containing a trace of certain aromatic compounds in solution. Applied as a zone reaction, the following colorations are obtained: *Gallic acid*, a reddish-brown ring, and, on shaking the tube, a green liquid changing to greyish-green. *Tannic acid*, a reddish-brown ring, and a liquid bluish-green at the bottom, but subsequently brownish-red throughout. *Pyrogallol*, a light rose-coloured ring, and liquid. The test is capable of detecting 0·00001% of formaldehyde. *Salicylic acid*, a light rose-coloured ring and solution. *Catechol* and *resorcinol*, various red rings and liquids. *β-Naphthol*, a violet-red ring, and brownish-black liquid with green fluorescence. *Benzonaphthol*, similar colour reactions. *Phenyl salicylate*, carmine-red ring and reddish-yellow liquid, becoming pink on dilution. *Phenolphthalein*, no ring, but an orange liquid changing to carmine-red on shaking. Dilution with water causes a carmine-red precipitate to separate.

C. A. M.

Estimation of Formaldehyde in Blood. E. SALKOWSKI (*Biochem. Zeitsch.*, 1919, **97**, 129—135).—The protein of the blood is hydrolysed with gastric juice. The hydrolysed mixture is distilled and *N*/10-iodine added to the distillate. The residnal iodine is then titrated with thiosulphate. The formaldehyde found amounted to only 85·73% of the quantity added to the blood.

S. S. Z.

Estimation of Acetone and Acetoacetic Acid with Autenrieth's Colorimeter. H. SCHALL (*Münch. med. Woch.*, 1919, **66**, 812—814; from *Chem. Zentr.*, 1919, iv, 562).—Description of the application of Autenrieth's colorimeter to the colorimetric estimation of acetone according to Legal and to the estimation of acetoacetic acid. Gerhardt's iron chloride reaction is suitable for the estimation of considerable concentrations of the latter (above 0·5%), whilst, at greater dilutions, Rimini's ethylenediamine test is used. The former has the advantage of easy manipulation and constancy of colour, whilst the latter is more sensitive and gives a pure tint which, however, rapidly loses in intensity. Empirical solutions of dyes are used as standards. When acetone and acetoacetic acid are present simultaneously, the estimation of acetone requires

the correction of a factor, since acetoacetic acid gives a positi Legal's reaction which is 5·55 as intense as that of acetone.

H. W.

An Acetoneurometer. A. Adler (*Münch. med. Woch.*, 191 **66**, 722—723; from *Chem. Zentr.*, 1919, iv, 398).—A colorimet method of estimating acetone is described which is based on Lega test. A mixture of urine (10 c.c.), sodium hydroxide solution (20 1 c.c.), and sodium nitroprusside solution (33%, 0·5 c.c.) is w shaken, and acetic acid (20 drops) is added. The colour is compar with that given by mixing Neutral-red, New-blue, and Diamon phosphine. Solutions of the dyes of the following concentrations a prepared: Neutral-red, 1:1000; New-blue, 1:1000; Diamond-pho phine D, 1:100. Ten c.c. of the first, 3 c.c. of the second, a 0·6 c.c. of the third solution are mixed with water, 5 c.c. (sol tion I), and correspond with 0·1% of acetone. Ten c.c. of solution diluted with an equal volume of water correspond with 0·08% acetone; 5 c.c. of solution I with 10 c.c. of water are equivalent i colour to 0·05% of acetone; 5 c.c. of solution I with 15 c.c. of wat correspond with 0·01% of acetone. Five c.c. of a solution of neutra red (10 c.c.), new-blue (1 c.c.), and diamond-phosphine (0·1 c.c with water (50 c.c.) correspond with 0·005% of acetone. The sol tions are placed in tubes similar to those used in the experimen which are subsequently sealed. The five standards are in practic sufficient for ascertaining the acetone content of a urine. H. W.

Methylene-blue as a Reagent for the Detection of Suga in Urine. F. Utz (*Süddeut. Apoth. Zeit.*, 1919, **59**, 280—281 from *Chem. Zentr.*, 1919, iv, 212—213).—According to the author' observations, urines which contain sugar always give a positive rea tion with solutions of methylene-blue, even when Lieber's modifica tion of the test is used. Aqueous solutions of dextrose behave simi larly, but sucrose, carbamide, uric acid, and saliva do not give th reaction. Milk behaves similarly to urine containing sugar. Whils aqueous solutions of hexamethylenetetramine do not react wit methylene-blue, the urines of patients to whom the drug has bee administered behave similarly to saccharine urines, but do not giv a positive result with Fehling's solution or Nylander's reagent Normal urines, free from sugar, also give a positive reaction wit methylene-blue when they have been preserved for some days an are partly decomposed, and this is particularly noticeable if the have been rendered alkaline with potassium hydroxide. Artificia gastric juice and glycuronic acid are also able to decoloris methylene-blue. The substance, therefore, is not a suitable reagen for the detection of sugar in urine. H. W.

Rapid Method for the Estimation of Sugar in Urine. Otto Mayer (*Arch. Hyg.*, 1919, **88**, 184—197; from *Chem. Zentr.*, 1919, iv, 211—212).—The detection of sugar in urine is best carried out by Trommer's test, for the performance of which, as also for Fehling's and Nylander's reactions, practical directions are given.

'he estimation of sugar is effected in the following manner: urine 10 c.c.) is placed in a 100 c.c. stoppered measuring cylinder, sodium ydroxide (15%, 10 c.c.) is added, and the solution is diluted to 0 c.c. with water; copper sulphate solution (25 grams per litre) is radually added with gentle shaking until the precipitate, which enotes the end of the reaction, practically completely redissolves n vigorous agitation, leaving only a just perceptible but permanent urbidity, which slightly increases in course of time. Under these onditions each c.c. of copper sulphate solution corresponds with ·1% of dextrose. If the urine contains more than 4% of sugar it s preferable to take only 5 c.c., whilst if the content is 0·5—1% 0 c.c. may be measured out. Separation of alkaline earth phoshates from urines which have been treated with alkali and diluted rom 2·5 to 10 times occurs only when these are present in exceptional quantity. In this case, since the sensitiveness of the endoint may be greatly reduced, it is advisable to treat 20 c.c. of the rine with 20 c.c. of sodium hydroxide solution, to filter the solution fter dilution to 100 c.c., and to perform the titration with 50 c.c. f the clear filtrate.

For the detection of acetone, powdered sodium nitroprusside 0·05—0·1 gram) is shaken with about 10 c.c. of urine, about 1 c.c. f sodium hydroxide (15%) is added to the solution, which is then cidified with acetic acid (30%, 2 c.c.). In this form the test is so ensitive that distillation is only necessary with such urines as are leeply coloured or contain only small amounts of acetone. The most nitable reagent for the detection of acetoacetic acid is a mixture of iquor ferri. sesquichl. (5 c.c.) and sodium chloride solution (1:3, 5 c.c.), the reaction being performed as a ring test. H. W.

Volumetric Estimation of Sugar in Milk. J. L. Mayer *J. Amer. Pharm. Assoc.*, 1919, **8**, 551—553).—Benedict's method or the estimation of dextrose in urine as modified by the author vas applied to the estimation of lactose in milk. The results were rustworthy. Chemical Abstracts.

[Estimation of Invert-sugar by Fehling's Solution.] J. D. van Leeuwen (*Chem. Weekblad*, 1919, **16**, 1425—1426).—In the itration of invert sugar solution with Fehling's solution, dilution of the latter with four times its volume of magnesium sulphate olution (0·5 gram per litre) causes the precipitated cuprous oxide o settle rapidly, and thus gives a clear solution for testing with otassium ferrocyanide and acetic acid; the solution must be cooled or this test. W. J. W.

Estimation of Carbamide by means of Sodium Hypobromite. E. Dekeuwer and L. Lescoeur (*Compt. rend. Soc. Biol.*, 1919, **82**, 445—447; from *Chem. Zentr.*, 1919, iv, 350).—In the stimation of pure carbamide by bromine and alkali hydroxide, a light deficit is always observed which has about the same magniude when calculated from the nitrogen evolved or from the bromine used; the error is doubled when the calculation is based on the

amount of carbon dioxide formed. The course of the reaction appears to depend on the relative quantities of alkali and carbamide. A factor can be applied based on the results obtained. In the estimation of carbamide in urine, high results are obtained when the calculation is based on the bromine which is utilised (particularly in the case of urines containing sugar), since bromine is also used in the oxidation of substances other than carbamide. The results deduced from the amounts of nitrogen and carbon dioxide formed respectively generally agree well among themselves; in the case of urines containing sugar, the values calculated from carbon dioxide are lower than those reckoned from nitrogen.

H. W.

Estimation of Carbamide in Blood and Urine. C. BRAHM (*Deut. med. Woch.*, 1919, **45**, 803; from *Chem. Zentr.*, 1919, iv, 442).—A criticism of Citron's method of estimating carbamide. The latter is not quantitatively decomposed by sodium hypobromite according to the scheme: $CO(NH_2)_2 + 3NaBrO = 3NaBr + CO_2 + 2H_2O + N_2$, since a proportion of the nitrogen is retained as nitric acid or cyanuric acid. In the author's opinion all methods which are based on the reaction between carbamide and sodium hypobromite are to be rejected. The form of apparatus proposed is also open to many objections. H. W.

Estimation of Carbamide in Urine by means of Urease. ARNOLD HAHN (*Deut. med. Woch.*, 1919, **45**, 911—912); from *Chem. Zentr.*, 1919, iv, 562—563).—The author's method has been modified by Horváth and Kadletz by the introduction of a receiver containing acid; the alteration is regarded as adding an unnecessary complication to the process. H. W.

Detection of Hydrocyanic Acid in a Case of Poisoning. Its Post-mortem Transformation into Sulphocyanic Acid. L. CHELLE (*Compt. rend.*, 1919, **169**, 852—854. Compare A., 1919, ii, 529, 530).—A dog was poisoned by administering potassium cyanide and an autopsy immediately performed, the various organs being divided up and kept in stoppered sterile flasks for various lengths of time. Using the methods previously described (*loc. cit.*), hydrocyanic acid as such, but no thiocyanic acid, was detected after two hours in the brain, lungs, and blood, but not in the liver. After eight days no hydrocyanic acid as such could be detected in any of the organs or the blood, but thiocyanic acid was found in the blood, lungs, and brain, but not in the liver. Further, the amount of thiocyanic acid found in the lungs and brain, but not in the blood, corresponded with far more than the amount of hydrocyanic acid found at the end of two hours. This is explained on the grounds that a certain amount of hydrocyanic acid becomes enclosed in the cells in the first few hours after death and is not set free by the methods of estimation used, but after eight days, as a result of

ıtrefaction and consequent cytolysis, it is all liberated by the agents and thus estimated. W. G.

Estimation of Ferricyanide and Ferrocyanide. I. M. OLTHOFF (*Pharm. Weekblad*, 1919, **56**, 1618—1626).—The author ıs investigated the iodometric estimation of potassium ferricyanide. ıe acidity of the solution has an appreciable influence on the action; if the concentration is sufficiently high, accurate results e obtained after allowing the solutions to remain for only half a inute. Rupp's method for the estimation of ferrocyanide is inac-.rate. An outline is given of the theoretical interpretation of the dometric estimation of ferri- and ferro-cyanide. The reducing tion of ferrocyanide is increased by rise of temperature.

W. J. W.

Proteinogenous Amines. II. A Micro-chemical Colori-etric Method for Estimating Iminazole Derivatives. ARL K. KOESSLER and MILTON T. HANKE (*J. Biol. Chem.*, 1919, 9, 497—519).—The method depends on the colour reaction tween compounds containing the iminazole ring and sodium diazobenzenesulphonate. It can be applied directly to practic-ly any iminazole derivative, gives equally good results whether plied to pure solutions or mixtures, and is capable of estimating th a fair degree of accuracy as little as 0·00001 gram of any of e iminazoles. The iminazole derivative is added under certain nditions to a mixture of sodium carbonate and the *p*-diazo-nzenesulphonic acid in one cup of a Duboscq colorimeter, and e height of liquid in this cup is set at 20 mm. The other cup filled with an appropriate indicator solution, and the height ried until the colours match. From tables which have been pre-.red, the amount of the iminazole derivative can be read off. rtain substances interfere with the method, notably ketones, cohols, ammonium salts, and proteins. Animal charcoal must t be used to decolorise solutions which it is desired to test for inazole derivatives, as loss by adsorption occurs. J. C. D.

Proteinogenous Amines. III. A Quantitative Method r Separating Histamine from Histidine. KARL K. KOESSLER d MILTON T. HANKE (*J. Biol. Chem.*, 1919, **39**, 521—538).—ıe colorimetric process described in the preceding abstract may utilised for estimating certain components of mixtures of inazole derivatives. A mixture of these derivatives, such, for ample, as that which is formed by the action of bacteria on ıtidine in the presence of salts and dextrose, is treated with ficient sodium hydroxide to make the whole a 20% solution of ali. This solution is extracted repeatedly with amyl alcohol, ereby the histamine, ammonia, methyliminazole, and other ıines are removed. This extract is termed the histamine frac-n, whilst the residual liquid containing histidine, iminazole, pro-nic, acetic and lactic acids is called the histidine fraction. The ıount of histidine can be determined by an estimation of the

amino-nitrogen in the second fraction. A colorimetric estimation on the same fraction will indicate whether there are other iminazole derivatives present other than histidine.

The histamine and methyliminazole are extracted from the amyl alcohol by 1·0*N*-sulphuric acid, and a colorimetric estimation will give on this extract an indication of the total iminazole substances present. The methyliminazole may be estimated directly by the fact that it is volatile in steam. The colorimetric estimations on these two fractions will give by difference the amount of histamine present. J. C. D.

Direct Estimation of Non-amino-nitrogen in the Products of Protein Hydrolysis. ALMA HILLER and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1919, **39**, 479—488).—An extension of the method of protein analysis introduced by Van Slyke (A., 1915, ii, 851). The filtrate from the phosphotungstates of the diamino-acids, representing 2 or 3 grams of protein, is concentrated to 150 c.c. Portions of this solution are used for estimations of the total nitrogen and amino-nitrogen, as described in the original paper. Of the residue, 100 c.c. are measured into a separating funnel of 500 c.c. capacity, and are rendered free from phosphotungstic acid by extraction with amyl alcohol–ether mixture in the presence of hydrochloric acid. The solution is concentrated in a vacuum to about 50 c.c., and washed into a 100 c.c. volumetric flask. Of this solution, 20 c.c. portions are used for the non-amino-nitrogen estimation. Each portion is placed in a small Kjeldahl flask with 1·2 c.c. of 30% sodium nitrite and 5 c.c. of concentrated hydrochloric acid. When deamination is completed, the solution is neutralised to alizarin with 10% sodium hydroxide and reduced with zinc–copper couple. After making alkaline with magnesium oxide, the ammonia formed by the reduction is removed by boiling and residual nitrogen is estimated by the Kjeldahl process. The results by this direct method agreed closely, in analyses of caseinogen and gelatin, with the results obtained indirectly by the original procedure. J. C. D.

Apparatus for Rapid Gastric Analysis, together with a Method for the Preservation of Starch Solution. RAYMOND J. MILLER (*J. Ind. Eng. Chem.*, 1919, **11**, 963—964).—A convenient arrangement of burettes, indicator reservoirs and delivery tubes, an automatic pipette, etc., attached to one stand and intended for the estimation of total acidity, free acidity, and amino-acid nitrogen (formaldehyde method) in gastric fluids. The starch solution is preserved under a layer of liquid "petrolatum," with or without the addition of a small quantity of toluene.

W. P. S.

General and Physical Chemistry.

The Constitution of the Atom and the Properties of Band Spectra. H. DESLANDRES (*Compt. rend.*, 1919, **169**, 1365—1371. Compare A., 1919, ii, 206, 310, 441, 486).—Further evidence is given in support of the views previously published (*loc. cit.*). The author emphasises the fact that the formula given (A., 1919, ii, 206, 310) is only a first approximation, and offers some explanation of the divergencies found in certain cases. W. G.

Intensity Relations in the Spectrum of Helium. T. R. MERTON and J. W. NICHOLSON (*Phil. Trans.*, 1919, *A*, **220**, 137—173).—The spectrum of helium has been examined by photographing the radiation in front of an aluminium cathode in a tube containing helium of such a pressure that the thickness of the dark space was about 1 mm. A number of experiments were made with mixtures of helium and other gases, particularly hydrogen. The most striking phenomenon observed relates to the difference in behaviour between the series of helium and parhelium, for, in the former, lines belonging to a series maintain a practically constant intensity ratio at every point, whilst in the latter the relative intensity of any two lines of the same series varies with the distance from the cathode. In the case of lines belonging to the principal series, the seat of maximum emission is closer to the cathode, and falls away with increasing distance from this point more rapidly than in the case of lines belonging to associated series. The diffuse series appear to preserve the most uniform intensity over a wide range of conditions. J. F. S.

Spectrum of Neon. F. PASCHEN (*Ann. Physik*, 1919, [iv], 60, 405—453).—An account is given of a very complete examination of the spectrum of neon from λ 9840·42 to λ 2550·55. A long table is given of the wave-lengths, intensities, and the spectrum combination of each line. The regularities between the lines of the principal and subsidiary series are investigated and discussed.

J. F. S.

Emission Spectra and the Chemical Reactions taking place in the Source of Radiation. ANGEL DEL CAMPO (*Anal. Fis. Quim.*, 1919, **17**, 247—270).—Attention is directed to slight variations in the spectrum of the same element as described by different observers. The author regards these as being due to chemical reactions, notably oxidation and reduction, occurring within the radiant arc. These reactions may be localised, according to circumstances, in the immediate neighbourhood of the electrodes or in the middle of the arc itself, thus giving rise to a "polar effect" in the photograph. This is illustrated in the case of the

silica spectrum, which shows variations as different sections of the arc between the carbon electrodes are examined. The view is expressed that the variations are due to the presence or absence of a reduction product, the suboxide SiO. A similar phenomenon is observed with magnesium, and is attributed to the suboxide Mg_2O. In studying the spectra of various specimens of aragonite, three new lines, 2554·6, 2563·8, and 2565·0 A.U., were observed. These were given by all samples of naturally occurring calcium carbonate examined, but not by pure hydroxide. In both cases the oxide formed is reduced to metal in contact with the carbon. This is immediately re-oxidised in the arc, but in the former case the protective action of the carbon dioxide liberated at the same time ensures the persistence of the metallic vapour for a longer time and range, so that the radiation from the metal is rendered perceptible. Further experiments confirmed the view that the lines in question belong to the calcium spectrum, and are not due to impurities in the substances examined. W. S. M.

The Emission of Positive Luminous Particles at High Temperatures by the Alkali Metals. G. A. HEMSALECH (*Compt. rend.*, 1920, **170**, 44—47).—Using the graphite plate with a layer of carborundum, the plate being electrically heated as previously described (compare this vol., ii, 1, 2), it is shown that if the plate is first covered with a thin layer of the chloride, carbonate, or oxide of one of the alkali metals, and this, in turn, covered with carborundum, positively electrified particles are emitted at varying temperatures. All the elements in the alkali group emit positive particles, and for a given temperature the extension and development of the luminous trajectories vary directly with the atomic weights, and in consequence the critical temperature, or temperature at which the phenomenon is apparent, varies inversely with the atomic weight. For lithium the critical temperature is 2700°, and for cæsium 1900°. Two hypotheses are put forward to explain this phenomenon, but further work is necessary before a definite explanation can be given. W. G.

[**The Emission of Positive Luminous Particles at High Temperatures by the Alkali Metals.**] A. DE GRAMONT (*Compt. rend.*, 1920, **170**, 47).—The author states that Hemsalech used a monochromatic, optical pyrometer for the temperature measurements in his work (preceding abstract). The instrument was calibrated and corrected up to 2500°, above which temperature extrapolation was necessary. At 2700° the temperature readings are accurate to ±50°. W. G.

The Direct Arc Spectra of Metals with Moderately High Melting Points. A. DE GRAMONT (*Compt. rend.*, 1920, **170**, 31—38).—A comparison of the direct arc spectra with the spark spectra and the carbon arc spectra in the case of the metals zinc, cadmium, tin, lead, antimony, bismuth, magnesium, and aluminium. By the photographic device employed, the three spectra were obtained in

successive coincidence, thus permitting of a direct comparison of the rays. By this means, it has been possible to detect in the direct ray spectra on the one hand certain rays of the spark spectra, considered by Lockyer as strengthened, and which occur in the direct spectra with a marked intensity, and on the other certain rays of the spark spectra, also classed as strengthened, but which are only fugitive in the direct arc spectra. The latter group of rays appears at the positive pole at the moment of striking the arc. They can most easily be seen by alternately making and breaking the arc. The detailed results are given for each of the metals, and the general conclusions to be drawn are that the arc spectra must not be considered as invariable and always identical. They are subject to considerable variations, not only in the intensities of certain rays, but also in the appearance of the rays, these variations being closely connected with the intensity of the current producing the arc. W. G.

New Lines in the Arc Spectrum of Silver between λ 4500 and λ 2300. M. A. CATALÁN (*Anal. Fis. Quim.*, 1917, **15**, 483—486).—Measurements of eighty new lines were made with wave-lengths corresponding with similar lines in the spark spectrum described by Exner and Haschek ("Tabellen der Funkenlinien," 1902). W. S. M.

New Lines in the Arc Spectrum in Air of Iron between 2300 and 1980 Å.U. S. PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1917, **15**, 434—444).—Measurements of more than 288 new lines in the arc spectrum of iron are given, extending the spectrum from 2300 Å.U. to 1994 Å.U. W. S. M.

New Lines in the Arc Spectra of Nickel and Cobalt between 2300 and 2000 Å.U. S. PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1918, **16**, 338—350).—A total of 66 new lines for nickel and 165 for cobalt in the given range was measured. W. S. M.

Photochemistry of Thallous Chloride. CARL RENZ (*Helv. Chim. Acta*, 1919, **2**, 704—717).—The action of light on thallous chloride has been investigated; the action was carried out with the dry substance and with thallous chloride under water, hydrochloric acid, ammonia, ethylamine, ethyl alcohol, glycerol, toluene, xylene, and pyridine. In all cases, a darkening occurs, which passes through the shades greyish-brown, dark greyish-brown, and blackish-brown. The change is due to the formation of a photothallous chloride and thallous-thallic chloride. Hydrochloric acid, even in traces, retards the formation of the photo-chloride, and, after prolonged illumination, various yellow, double thallous-thallic chlorides are formed. Nitric acid and sulphuric acid have a similar retarding action on the formation of the photo-chloride. Ammonia, ethylamine, and the above-named organic substances act as sensitisers in the reaction, and many inorganic salts have a photo

catalytic action. The sensitiveness of thallous chloride to light depends on its method of formation. Thallous chloride precipitated by metal chlorides is more sensitive than that precipitated with hydrochloric acid, even though the acid has been thoroughly washed out. J. F. S.

Diffusion of Radium Emanation in Water. EVA RAMSTEDT (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 5, 1—14).—The velocity of diffusion of radium emanation in water at 14° has been determined by means of an apparatus containing a number of metal plates immersed in water. The coefficient of diffusion is found to be 0·820 cm. per day, a value which is of the same dimensions (0·985 at 18°) as that recently found by Rona (A., 1917, ii, 286). Calculating from this value, the product $D\sqrt{m}$ is found to be 12·2, and the molecular diameter of radium emanation $1{\cdot}85 \times 10^{-8}$ cm. J. F. S.

Ionisation Potential of Helium. J. FRANCK and P. KNIPPING (*Physikal. Zeitsch.*, 1919, **20**, 481—488).—Using as source of electrons a glowing wire in helium of pressure 1·5 mm., the resonance potential is found to have the value 20·5 ± 0·25 volts, and from this value the ionisation potential is calculated to 25·3 ± 0·25 volts. Experimentally, the ionisation potential of helium is found to be 25·4 ± 0·25 volts, and the resonance potential has the same value as before. The potential necessary for the removal of both electrons from the helium atom is also determined, and the value 79·5 ± 0·3 volts obtained. The present results are in agreement with those of Horton and Davies (A., 1919, ii, 210), and indicate that the helium atom is much less stable than is indicated by the atomic model of Bohr and Landé. J. F. S.

Conductivity. VI. Behaviour of Mixtures of Two Salts containing a Common Ion in Anhydrous Formic Acid Solution. H. I. SCHLESINGER and F. H. REED (*J. Amer. Chem. Soc.*, 1919, **41**, 1921—1934. Compare A., 1919, ii, 91).—The conductivity of potassium formate in anhydrous formic acid solution has been determined at 25° over the range $0{\cdot}1207N$—$0{\cdot}3266N$. The degree of ionisation and the ionisation constant are calculated in each case, and the latter constant has the value 1·090. Similar measurements were also made for sodium formate and lithium formate; these salts have ionisation constants 0·810 and 0·557 respectively. Conductivity measurements were also made for mixed solutions of sodium and potassium formates, lithium and potassium formates, strontium and potassium formates, and strontium and calcium formates, all in anhydrous formic acid and at 25°. A method of calculating from the ionisation constants the degree of ionisation of each of two salts containing a common ion, when the two salts are both present in solution, has been developed for the case in which both salts obey the law of mass action. It is found that in mixtures of sodium and potassium formates, as

well as of lithium and potassium formates, the mass law is obeyed by both of the highly ionised salts present. On the other hand, solutions of mixtures containing, as one or as both of the salts, alkaline earth formates do not conform to the law, although these uni-bivalent salts when in solution alone seem to follow the law over a certain range of concentration. This appears to make it quite certain that whenever the agreement of the salt with the law is an accidental one, solutions of mixtures containing such a salt will not obey the law. Hence it may be definitely concluded that the agreement between the behaviour of the alkali metal formates, in anhydrous formic acid solution, and the demands of the mass law is a real and not an accidental one. When the total concentration of mixed solutions becomes relatively great, deviation from the mass law occurs also in the solutions which contain uni-univalent formates. It has been found that this deviation begins when the concentration of the non-ionised molecules of one of the salts reaches the same value as that at which deviation begins in the solution of that salt by itself. This seems to be independent of the concentration of the other molecular species present, and to indicate that in concentrated solutions it is the non-ionised molecules, and not the ions, which cause deviation from the mass law, or at least the non-ionised molecules cause deviation at lower concentrations than do the ions. J. F. S.

Conductivity. VII. Transference Numbers of the Formates of Sodium, Potassium, and Calcium in Anhydrous Formic Acid. H. I. Schlesinger and E. N. Bunting (*J. Amer. Chem. Soc.*, 1919, **41**, 1934—1945. Compare preceding abstract).—The transport numbers of solutions of sodium, potassium, and calcium formate in anhydrous formic acid have been determined by the usual method at 25° for a number of concentrations between 0·09*N* and 0·4*N*. The ionic conductivity of the formate ion is calculated to be 51·5, that of sodium ion 14·6, and potassium 17·5. The transport number of the potassium ion changes with concentration. This is tentatively explained on the assumption that the ion is solvated, and a method for calculating the extent of solvation from the transport numbers is suggested. The results indicate that, if the assumptions made in the calculation are correct, each potassium ion is combined with from six to eight molecules of formic acid. The transport numbers obtained for calcium formate do not substantiate the view that calcium formate in formic acid solution ionises either entirely as a uni-univalent salt or entirely as a uni-bivalent salt. It is therefore possible that both methods of ionisation occur. J. F. S.

Electric Conductivity of Weakly Ionised Neutral Salts. Olof Svanberg (*Medd. K. Ventenskapsakad. Nobel-Inst.*, 1918, **3**, No. 26, 1—7).—The equivalent conductivity of potassium antimonyl tartrate and cupric acetate has been determined over the range *N*/4 to *N*/1024 at temperatures 0—65°. In the case of potassium antimonyl tartrate the equivalent conductivity increases from 64·4 at

$d=4$ to 134·5 at $d=1024$ at 25°; the more concentrated solutions (up to $N/32$) at all temperatures follow the Ostwald dilution law, but beyond this point the conductivity increases more rapidly than is demanded by any of the formulæ for the extrapolation of the infinity value. There is no evidence that potassium antimonyl tartrate ionises as the potassium salt of antimonyl tartaric acid, and it is also shown that the salt is not greatly hydrolysed in any of the solutions examined. In the case of cupric acetate the equivalent conductivity at 25° increases from 10·8 in N-solutions to 75·3 in $N/1024$ solutions, which indicates considerable hydrolysis. The equivalent conductivity at infinite dilution has been obtained by extrapolation, and the following values found: potassium antimonyl tartrate, 0°, $\Delta_{\infty}=76$; 25°, $\Delta_{\infty}=154$; 50°, $\Delta_{\infty}=260$; 65°, $\Delta_{\infty}=308$, copper acetate, 25°, $\Delta_{\infty}=90$. J. F. S.

Relation between the Electrical Phenomenon in Cloud-like, Condensed, Odorous Water Vapours and Smell-intensity. H. Zwaardemaker and H. Zeehuisen (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 175—178).—Odorous organic substances in dilute aqueous solution when sprayed yield electric charges. It is found on diluting these solutions to such an extent that the electrical phenomena are only just appreciable that the odour is also just appreciable. It is suggested that both these properties depend in a complicated way on (*a*) the volatility of the substances, and (*b*) the lowering of the surface tension of the solvent (compare A., 1918, ii, 351). J. F. S.

Dielectric Constants considered in Connexion with the Theory of Dipolar Molecules. Oskar Klein (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 24, 1—48).—The dielectric constants have been determined for a number of solutions in organic liquids by means of a resonance method. The solutions examined consisted of (1) methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, amyl alcohol, allyl alcohol, benzyl alcohol, acetone and methyl ethyl ketone in benzene; (2) ethyl alcohol, butyl alcohol, and benzyl alcohol in chloroform. It is shown that the resonance method, which is the method used technically for measuring capacity, is well suited to the measurement of dielectric constants. Solutions of the alcohols in benzene or chloroform of the same normality have the same dielectric constant. Thus N-solutions of alcohols in benzene have a dielectric constant 2·63, in chloroform solution 5·68. Acetone and methyl ethyl ketone have the same value in benzene solution, namely, 3·09. J. J. Thomson's rule that related substances have the same value for $(\epsilon-1)M$ holds absolutely for mixtures of the alcohols and water. Some measurements of Pohrt on the dielectric constants of gases are examined, and yield the temperature-coefficient which is demanded by the dipolar theory. The formula of Debye $(\epsilon-1)/(\epsilon+2)\,.\,v=A/T+B$ is changed to the form $(\epsilon-1)(v-b)=A/T$, in which for substances which belong to a single group the relationship $AM=L$ obtains; L is a constant pro-

portional to the square of the molecular moment, and M is the molecular weight. These formulæ combine the above-named rules and are in keeping with the dipolar theory. The constant L has been calculated from several of the experiments, and the values for alcohol (67,000) and acetone (180,000) obtained. The formula $(\epsilon-1)=A/T(v-b)$ is applied to the dependence of the dielectric constant on temperature in the case of water, and found to be in keeping with facts. The formula $K=L/T=M(v-b)(\epsilon_0-1)+\mu/[1+k(\epsilon_0-1)]$ holds for infinitely dilute solutions, and together with $(\epsilon-1)=A/(v-b)T$ furnishes an exact method for calculating the constants K and b. The approximate formula $K=\mu/[(1+k(\epsilon_0-1)]$ is deduced from the above, and allows the determination of K from a knowledge of the dielectric constant of solutions of the substances concerned. J. F. S.

Dielectric Constants of Typical Aliphatic and Aromatic Hydrocarbons, *cyclo*Hexane, *cyclo*Hexanone, and *cyclo*-Hexanol. THEODORE W. RICHARDS and J. W. SHIPLEY (*J. Amer. Chem. Soc.*, 1919, **41**, 2002—2012).—The dielectric constants of a number of hydrocarbons have been determined at 20°, except in the case of *cyclo*hexanol, which was determined at 25°, by a modified Nernst type of apparatus. The percentage error of the method was much decreased by the use of larger suitably balanced condenser troughs. The following values have been obtained as the mean of several concordant measurements: hexane, 1·876; heptane, 1·973; octane, 1·962; *n*-nonane, 1·967; δ-methyloctane, 1·967; β-methyloctane, 1·967; βζ-dimethylheptane, 1·987; βδ-dimethylheptane, 1·89; βε-dimethylheptane, 1·89; decane, 1·956; xylene (commercial), 2·375; *m*-xylene, 2·377; ethylbenzene, 2·482; *n*-propylbenzene, 2·364; cumene, 2·400; mesitylene, 2·356; *tert.*-butylbenzene, 2·384; *cyclo*hexane, 2·055; *cyclo*hexanone, 18·2; and *cyclo*hexanol, 15·0. The present results are in moderate agreement with the values of previous observers, although in many cases no previous measurement is on record. J. F. S.

Relation between the Specific Inductive Capacity of an Electrolyte and the Electric Potential of a Metal placed in it. D. L. ULREY (*Physical Rev.*, 1919, **12**, 47—58).—Attention is called to the inadequacy of the Nernst theory of the mechanism of galvanic current production. This theory omits an essential factor, namely, specific inductive capacity of the electrolyte, and employs two hypothetical quantities, metal solution pressure and osmotic pressure of the ions. Transfer of ions between metal and electrolyte is probably brought about by electrical forces, the magnitude of which depends on the specific inductive capacity of the medium. The potential difference between electrodes of the same kind in a two-solution cell was measured for several different percentage mixtures of two liquids for four different cases, and in each case was shown to be strictly proportional to the difference in the specific inductive capacity of the two solutions. The following systems were measured: (*a*) ethyl alcohol–water (solution of cupric

chloride), with copper electrodes (electrode in the aqueous solution electronegative); (*b*) ethyl alcohol–water, with calomel electrodes (electrode in the water electropositive); (*c*) acetone–water, with calomel electrodes (electrode in the water electropositive); (*d*) methyl alcohol–water, with calomel electrodes (electrode in the water electropositive); and (*e*) solution of carbamide–water, with platinum electrodes (electrode in the water electropositive). In two cases investigated with copper electrodes, one with platinum electrodes, and six with calomel electrodes, the direction of the *E.M.F.* of the cell is in accordance with the theory that the loss of ions from an electrode is dependent on the specific inductive capacity of the electrolyte rather than on the concentration of those ions in the electrolyte and a solution tension of the electrode. Results obtained further substantiate the theory that the more electropositive metals have the higher specific inductive capacities. CHEMICAL ABSTRACTS.

Changes of Potential in an Oxidising Agent by Ultra-violet Light. TORSTEN SWENSSON (*Arkiv. Kem. Min. Geol.*, 1917, **6**, No. 12, 1—32).—The effect of ultra-violet light on the potential of solutions of potassium dichromate in sulphuric acid has been examined. The source of light employed was a quartz mercury lamp, and the solutions were maintained at 18° during illumination. The platinum electrode used in the measurements was bright, since it was found that the same value was obtained with both bright and platinised electrodes, but the former reached equilibrium more rapidly. It is shown that during the illumination with ultra-violet light of a solution of potassium dichromate and sulphuric acid, and also during the illumination of either sulphuric acid, potassium dichromate, or chromic acid alone, a change in potential occurs. To achieve this result it is not necessary to illuminate the platinum electrode. In the case of dichromate and sulphuric acid a speedy increase in the potential occurs; whilst when sulphuric acid and dichromate are illuminated separately a decrease in potential occurs. The potential is also decreased for pure chromic acid, and consequently it is shown that the positive effect does not depend on the liberation of this acid on the addition of sulphuric acid to the dichromate. The speedy change in *E.M.F.* is caused by the ultra-violet rays, and is not observed when the action takes place in glass vessels. Both the increase and decrease of *E.M.F.* are of a photochemical nature. Over the range examined the potential change is independent of dilution. The change of potential is in a high degree dependent on the composition of the solution, and shows a maximum at about 75 mol. % potassium dichromate. The decrease in *E.M.F.* after the interruption of the illumination takes place gradually. It is also dependent on the composition, and is most rapid for pure sulphuric acid. It is further greatly dependent on the temperature, and after a moment's boiling the potential becomes normal again. Solutions which have been illuminated, but have returned to their original potential, show on renewed illumination changes in the velocity of the potential

increase and the maximum value. On very bright illumination a rapid increase in *E.M.F.* was observed, which, on interruption of the light, sank very quickly. In this case the illumination of the electrode is essential. J. F. S.

Polarisation Tensions of Iron in Solutions of its Complex Salts. Relations between these Tensions and the Dissimulation of Analytical Characters of Ferric Ions. N. R. Dhar and G. Urbain (*Compt. rend.*, 1919, **169**, 1395—1397).—The electrolytic cell consists of two half elements joined by a solution of potassium chloride. One half element consists of a metallic electrode in a solution of one of its salts, and the other is an electrode of mercury in a solution of calomel and potassium chloride. The polarisation tension is defined as the difference between the *E.M.F.* of the whole cell and the corresponding value as found in Auerbach's results (compare A., 1912, ii, 123) for the half element containing the mercury electrode. This tension should depend on the number of free metallic ions in the solution, the tension diminishing as the number of ions increases. These measurements should, therefore, in the case of complex salts, give an indication as to how far the metallic constituent of the complex ion is dissimulated. The results obtained with simple and complex iron salts are in agreement with those obtained by Pascal (A., 1909, ii, 487) as to their molecular magnetic susceptibilities. W. G.

Hydrogen Overvoltage. II. Applications of its Variation with Pressure to Reduction, Metal Solution, and Deposition. D. A. MacInnes and A. W. Contieri (*J. Amer. Chem. Soc.*, 1919, **41**, 2013—2019. Compare A., 1919, ii, 131).—The increase of hydrogen over-voltage with diminished pressure is shown to follow, in a nearly quantitative manner, from the theory of MacInnes and Adler (*loc. cit.*). The effect of a change in the gaseous pressure on several chemical processes involving the evolution of hydrogen has been studied. The changes in rates of reaction and in reaction efficiencies were found in each case to be in the directions which follow from the change of hydrogen over-voltage with pressure; that is, a decrease of gaseous pressure produces (*a*) a decrease in the rate of solution of metals in electrolytes, (*b*) an increase in the efficiency of reductions by metals, and (*c*) an increased efficiency of metal deposition. The theory explaining the fluctuation of over-voltage accompanying the evolution of a single bubble of hydrogen from a platinum electrode is discussed. J. F. S.

Determination of the Hydrogen Exponent. J. Pinkhof (*Chem. Weekblad*, 1919, **16**, 1168—1172).—If, in Poggendorff's method, the normal electrode is replaced by an electrode which does not differ in potential from that of the hydrogen electrode, then, if the composition of the liquid is known and its relation to the potential, the potential of the hydrogen electrode, and therefore the hydrogen exponent, can be determined. The results obtained with a silver electrode in a solution of silver cyanide in

excess of potassium cyanide were not accurate. An electrode of cadmium amalgam in solutions of cadmium salt of various concentrations was found to be suitable. A simple apparatus for the determination is described. W. J. W.

Applicability of the Gas Laws to the Strong Electrolytes. J. N. Brönsted (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 25, 1—19).—*A number of solubility and E.M.F. measurements have been carried out with the object of testing the hypothesis.* "The gas laws hold for ions or salts when other salt solutions are employed as solvents, the concentration of the latter being large when compared with the concentration of the dissolved salt." The *E.M.F.* of cadmium | cadmium sulphate in magnesium sulphate solution has been measured. The element is made up:

$$\begin{array}{c|c|c|c} \text{Cd} & CdSO_4\ c\ \text{Mol.} & CdSO_4\ c_1\ \text{Mol.} & \text{Cd} \\ (\text{amalgam } 3\cdot1\%) & MgSO_4(2-c)\ \text{mol.} & MgSO_4(2-c_1)\ \text{mol.} & (\text{amalgam } 3\cdot1\%) \end{array}$$

The value of c and c_1 varied between $0\cdot1M$ and $1/640M$, and the temperature was 20° and 39·4°. The potentials obtained are compared with those demanded by the gas laws, and an excellent *agreement found. The solubility of dinitrotetra-amminecobalt* nitrate, both α and β varieties, has been determined at 0° and 20° in water, and in solutions of various concentrations of potassium formate, thiocyanate, hydroxide, and nitrate, nitric acid, sodium oxalate, and sodium nitrate. The values obtained are in keeping with the demands of the gas laws. J. F. S.

The Electroaffinity of Aluminium. I. The Ionisation and Hydrolysis of Aluminium Chloride. II. The Aluminium Electrode. Jaroslav Heyrovský (T., 1920, **117**, *11—26, 27—36*).

Occlusion of Hydrogen and Oxygen by Metal Electrodes. Edgar Newbery (*J. Amer. Chem. Soc.*, 1919, **41**, 1887—1892, *1895—1898*); Earle A. Harding and Donald P. Smith (*ibid.*, 1892—1894, 1897—1898).—Polemical. In the first paper Newbery gives a theoretical discussion of the paper put forward by Harding and Smith (A., 1918, *ii*, 424), and a *criticism of the theory put* forward as to the condition of the occluded hydrogen in palladium. The following papers contain replies and counter-replies by Harding and Smith, and Newbery. J. F. S.

Electro- and Thermo-chemical Investigation of the Cells Cu or Cu Amalgam | $CuSO_4$-Hg_2SO_4 | Hg. L. W. Öholm (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 4, 1—20). —The *E.M.F.* of the elements Cu | N-$CuSO_4$,Hg_2SO_4(sat.) | Hg and Cu(12% amalgam) | N-$CuSO_4$,Hg_2SO_4(sat.) | Hg have been measured *at 10°, 15°, 17°, 20°, 25°,* and 30° *daily for a period of two months.* The copper amalgam cells are fairly constant and easily reproducible, and the variation of the *E.M.F.* with temperature is represented by the formula

$$E_t = 0\cdot35030 - 0\cdot00064(t-20) - 0\cdot0000025(t-20)^2.$$

The cells with a copper electrode had a slightly higher (0·004—0·005

volt) *E.M.F.* than the amalgam cells, and it is nothing like so constant. $E_{20}=0\cdot3542$ and $dE/dT=-0\cdot00072$ volt. The chemical energy of the copper cell is calculated, and the value $Q=24,860$ cal. obtained. The quantity Q is regarded as made up of three quantities, q_1, q_2, and q_3, q_1 being the heat change when 1 gram-atom of copper is withdrawn from the amalgam, q_2 the difference in the heat of formation of copper and mercury sulphate, and q_3 the heat change accompanying the withdrawal of water from the solution by the newly formed copper sulphate. These three values are calculated to $q_1=-1297$ Cal. at 20°, $q_2=7600$ Cal., and $q_3=18\cdot527$ Cal.

J. F. S.

Passivity of Cobalt. HORACE G. BYERS and CURTIS W. KING (*J. Amer. Chem. Soc.*, 1919, **41**, 1902—1908).—When cobalt is used as anode in the electrolysis of $0\cdot02N$-sulphuric acid or sodium sulphate at 0°, it becomes passive if a high current density is employed, but with low current density it remains active; if potassium dichromate is present, it readily assumes the passive condition in all circumstances. The passive state is indicated by an increased drop in potential, a decreased current, by the evolution of oxygen, and by the failure of the cobalt to pass into solution. The potential measurements of a cobalt–platinum cell with various electrolytes, and a comparison with similar results with iron and nickel, show that when the cobalt becomes passive there is a marked increase in voltage across the cell. The potential measurements show that this is due to a change in the potential of cobalt as it changes from the active to the passive condition. Cobalt may therefore be classified with the passive metals, since it exhibits all the characteristics of iron and nickel when they are passive. The essential difference between cobalt and the other passive metals lies in the fact that cobalt, when used as an anode, will not become passive at the low current densities required by nickel and iron. If cobalt has once assumed the passive condition, it will remain so, even though the current density is reduced. In the absence of the anodic relation, cobalt becomes active in acid solution more readily than nickel.

J. F. S.

Activity Coefficient for Ions. NIELS BJERRUM (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 16, 1—21).—A theoretical paper in which activity coefficients are considered with the object of bringing strong electrolytes into line with the ionic hypothesis. The *activity coefficient* is defined as the effect of the interionic forces on the activity of the ions, the *conductivity coefficient* as the influence of the interionic forces on the conductivity, and the *osmotic coefficient* as the influence of the interionic forces on the osmotic pressure. Various relationships between these and other similar coefficients are evolved mathematically.

J. F. S.

Comparative Electrolysis of Various Alkali Chlorides. E. BRINER, (MLLE.) A. TYKOCINER, and B. ALFIMOFF (*Helv. Chim. Acta*, 1919, **2**, 666—672).—Solutions of the chlorides of sodium,

lithium, and potassium of various concentrations have been electrolysed, and the relative current yields of alkali hydroxide compared. After the passage of 50,000 coulombs through $3 \cdot 1N$-solutions of these salts, it is shown that the total current yields are respectively for lithium, sodium, and potassium 75%, 82·5%, and 87%. In the case of lithium chloride, two cases are considered: (*a*) Where the initial concentration of lithium chloride lies on the ascending branch of the conductivity curve (concentrations below $5N$); here the fraction of the current carried by the lithium chloride diminishes, due to the presence of lithium hydroxide and to the reduction of the salt concentration. (*b*) Where the initial concentration lies on the descending branch of the conductivity curve (concentrated solutions); here the yield is diminished by the lithium hydroxide present, but it is increased by the fact that the reduction of the lithium chloride concentration brings with it an improvement of the conductivity of the salt. J. F. S.

The Transport Number of the Ions of Cadmium Iodide. GEORGES HEYM (*Ann. Physique*, 1919, [ix], **12**, 443—454).—From a series of measurements, it is shown that the transport number of iodine ions varies from 0·55 to 1·0 for solutions of cadmium iodide in which the concentration varies from 0·007 to 0·07 gram of iodine per litre. W. G.

Electrochemistry of Uranium and the Single Potentials of Some Oxides of Uranium. CHESTER A. PIERLÉ (*J. Physical Chem.*, 1919, **23**, 517—553).—The electrolysis of uranium compounds in various solvents and under many conditions has been investigated. It is shown that in aqueous solutions with low current density, uranyl salts deposit, in the first place, hydrated uranic oxide, UO_3,H_2O, which is changed as the electrolysis proceeds to a black oxide of varying composition. With higher current density, uranyl sulphate is reduced to uranous sulphate, but in the presence of free acid the deposit obtained is small in amount and poorly adherent, although metallic in appearance. In neutral or alkaline solutions, the deposit formed is a mixture of black and yellow oxides. The use of a porous cup diaphragm does not change the character of the deposits. The deposit obtained when alkaline uranyl tartrate or citrate solutions are electrolysed is an oxide much richer in uranium than that deposited from solutions acidified with tartaric or citric acid. The conductivity of non-aqueous solutions of uranyl salts is a function of the water present, and the deposits formed are oxides contaminated with organic matter. Anhydrous pyridine dissolves anhydrous uranium tetrachloride to form conducting solutions; these, on electrolysis, deposit a compound containing uranium and pyridine on the cathode. Solutions of uranium tetrachloride in acetone do not yield metallic uranium on electrolysis; the solution is a good conductor of electricity. The deposit obtained replaces mercury from mercurous sulphate. Uranium tetrachloride reacts with anhydrous acetone, forming ββ-dichloropropane. During electro-

lysis, hydrogen is evolved. Solutions of potassium uranyl fluoride, whether acid, alkaline, or neutral, form a deposit containing fluorine; in acid solution, the deposit is $UF_4,6H_2O$; neutral and alkaline solutions give a deposit containing uranium tetrafluoride and uranium oxide. Deposits obtained from neutral solutions of potassium uranyl cyanide consist of pure potassium uranate. When acidified with hydrocyanic acid, the deposit is the yellow, hydrated oxide contaminated with a little of the black oxide. The single potentials of the metal and the oxides have been measured by pasting the finely powdered material on a platinum electrode with gelatin. The following potentials of the more stable oxides have been obtained: $U_3O_8 | UO_2(NO_3)_2$, 14·3 grams per litre$\|$ = 0·776 volt; $UO_3,H_2O | UO_2(NO_3)_2 \|$ = −0·860; black oxide from aqueous uranyl salts$| UO_2(NO_3)_2 \|$ = −0·6872 volt; uranium 91·49% $| UO_2(NO_3)_2 \|$ = −0·093 volt. Uranous oxide, UO_2, gives a single potential identical with that obtained for the green oxide, U_3O_8. The black deposit formed when uranium salts are electrolysed is not $U_3O_8,2H_2O$, as stated by Smith (*Amer. Chem. J.*, 1879, **1**, 329), but a compound, $U_3O_{10},2H_2O$, and it has a different potential to that of U_3O_8. J. F. S.

Johan Gadolin's Electrochemical Theory, its Origin and Development. H. G. Söderbaum (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 9, 1—14).—Historical. T. S. P.

Diamagnetic Phenomenon in Luminous Nitrogen and the Magnetic Behaviour of its Band Spectrum. W. Steubing (*Physikal. Zeitsch.*, 1919, **20**, 512—519).—The intensity changes of the nitrogen bands in a magnetic field have been examined with the magnet in various positions. It is found that if a flat bulb 33 mm. in diameter is blown in the middle of the tube and the tube filled as for an ordinary spectrum observation, the light passes across the bulb in the ordinary way, except that the positive column is slightly broadened. When the field is made active the middle of the bulb is filled with a blue, luminous sheath, which extends up to the walls and is at right angles to the lines of force of the field. This sheath has an identical spectrum with the negative luminescence, and is probably to be accounted for by the diamagnetic molecules setting themselves at right angles to the magnetic lines. J. F. S.

Magnetic Properties of some Rare Earth Oxides at Low Temperatures. E. H. Williams (*Chem. News*, 1919, **119**, 287—288).—The magnetic susceptibility of the oxides of dysprosium, erbium, gadolinium, samarium, neodymium, lanthanum, and yttrium has been determined at a series of temperatures from 20° to −140°. The following values are given: Dysprosium oxide, 20°, $X \times 10^6$, 233·3°; 0°, 250·0; −40°, 291·3°; −80°, 347·4; −100°, 384·2; −120°, 430·2; −140°, 490·0. Erbium oxide, 20°, 188·6; 0°, 201·7; −40°, 234·8; −80°, 282·3; −100°, 314·8; −120°, 355·0; −140°, 402·8. Gadolinium oxide, 20°, 129·7; 0°, 138·2; −40°, 160·7; −80°, 194·2; −100°, 217·0; −120°, 244·6; −140°, 279·0.

In all cases the oxides were purer than 99·5%. In the case of samarium oxide the susceptibility at $-140°$ was about 10% larger than at 20°. Yttrium oxide increases in susceptibility with decrease in temperature, but very slightly, and since the susceptibility is less than 1×10^{-6} the experimental error is relatively large. It is shown that the product of the susceptibility and the absolute temperature is not constant, but decreases with falling temperature to a slight extent. J. F. S.

The Paramagnetism of Solid Salts and the Theory of the Magneton. B. Cabrera (*Anal. Fis. Quim.*, 1918, **16**, 436—449).—A mathematical discussion of the Curie-Langevin law when the mutual actions of the paramagnetic atoms are no longer negligible. W. S. M.

Furnace Temperature Regulator. Walter P. White and Leason H. Adams (*Physical Rev.*, 1919, **14**, 44—48).—By making the heating coil of an electric furnace one arm of a Wheatstone bridge, and combining this with a galvanometer regulator, thus keeping the resistance of the coil constant, the temperature of electric furnaces may be kept constant. This device is effective regardless of variations in the current supply, and requires no attention, particularly in the case of furnaces which are not directly influenced by the temperature of the room or where the surrounding air is kept constant. The arrangement operates as follows: Changes in the temperature of the furnace, and consequently in the resistance of the heating coil, operate a boom which either hits or misses a contact-maker which controls a suitable relay. This relay operates a larger magnet, which controls the main current. The power available in this regulator is very large; nothing has to be inserted into the furnace cavity, and the lag is practically non-existent. The regulator is often almost at its best under conditions most unfavourable to other regulators. Using this regulator, the authors have kept a small furnace constant to within 0·1° for hours at temperatures from 500° to 1400°. J. F. S.

***An Analysis of the Radiation Emitted in Gaseous* Explosions.** W. T. David (*Phil. Mag.*, 1920, vi, **39**, 84—95).—In explosions of coal-gas and air, and of hydrogen and air, the ratio of the energy in the 2·8 μ radiation emitted to that in the radiation of longer wave-length decreases as the temperature decreases. In the neighbourhood of 1200° abs. the 2·8 μ radiation decreases very rapidly with the temperature, and is negligible at 1000° abs. Radiation of longer wave-length is emitted after the temperature has fallen to 900° abs., but at this temperature the emission is small. The ratio of the energies in the 2·8 μ and the 4·4 μ radiation in coal-gas and air mixtures appears to depend on the composition of the mixture and the temperature. The loss of heat by radiation expressed as a percentage of the heat of combustion of hydrogen and air mixtures, between the limits of composition of 10 and 25·4% of combustible gas, decreases very rapidly as the latter increases.

The variation for mixtures of coal-gas and air between 9·8 and 15% is small. The author attempts a theoretical explanation of these results on the following lines. The intra-molecular energy acquired on combustion by the freshly-formed molecules of carbon dioxide and water is not equally partitioned over the various internal degrees of freedom of the molecules. When the combustion is gentle the intra-molecular energy is concentrated in the rotational degrees of freedom, and in such very low frequency vibrations as the molecules may be capable of executing. As the combustion becomes more violent the higher frequency vibrations share in this energy, and it is possible that during combustion of extreme violence equipartitioning of energy amongst all the internal degrees of freedom of the molecules may be approached momentarily. This is believed to be capable of explaining many phenomena of explosive combustion, such as the pre-pressure period. J. R. P.

Isothermals of Monatomic Substances and their Binary Mixtures. XX. Isothermals of Neon from 20° to −217°. C. A. CROMMELIN, J. PALACIOS MARTINEZ, and H. KAMMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 108—118. Compare A., 1917, ii, 407; 1918, ii, 9).—The isothermals of neon have been determined over the range 20° to −217° up to a pressure of 90 atms. by the method previously described. From the results of the experiments the authors have calculated the virial-coefficients from the equation of state. It is shown that the pv_A values obtained in the present work agree in a very satisfactory manner with the older measurements. Only in the isothermal −217·52° is any marked divergence visible, and here the divergence does not exceed 0·5%, whilst for the isothermal −200·08° they do not reach 0·1%. J. F. S.

A New Improvement of the Equation of State of Fluids. E. ARIÈS (*Compt. rend.*, 1919, **169**, 1140—1143).—A mathematical discussion of the subject. W. G.

Equation of Condition. FRED. G. EDWARDS (*Chem. News*, 1920, **120**, 4—5).—Using Nernst's value in the equation for the mean molecular heat of gases, $Cv=a+bt$, it is shown that these linear equations are chords to the curve $m^x=k \log T$, where $m=5{\cdot}95/y$ or $4-(2y/2{\cdot}975)$ below or above $y=2{\cdot}975$, from which is obtained the general equation $m^x=k/\log T=1/v \log T$, and hence $pv=m^xT$, m^x being a constant for monatomic gases. W. G.

Corrected van der Waals's Equation of Condition for the Quasi-diminution of the Molecule. E. A. HOLM (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 27, 1—33).—In the corrected van der Waals's equation an infinite series of b/v appears as the correction factor of the volume. This has been inserted by Boltzmann in an approximated form as $1-b/v+0{\cdot}375b^2/v^2-0{\cdot}0369b^3/v^3$. This cannot be true for very small volumes. The equation has been tested on Amagat's oxygen isotherms, and it is

found to be strictly applicable at pressures 250, 300, and 450 atm. and at temperatures 0°, 15·63°, 99·50°, and 199·5°. The negative divergence found for very high pressures is due entirely to the mathematical incompleteness of the formula. J. F. S.

Determination of Chemical Constants. ALFRED C. EGERTON (*Phil. Mag.*, 1920, [vi], **39**, 1—20).—The author emphasises the fact that the usual formula for the calculation of chemical constants from vapour pressures, due to Nernst, cannot give results having any theoretical significance, because the assumptions as to the specific heats at low temperatures which are contained in it have been shown to be incorrect by recent experiments. He therefore modifies the formula by substituting for these assumptions the more exact expressions for the specific heats of solids at low temperatures, and assumes that the atomic heats of gases remain constant and equal to $5/2 . R$ at the lowest temperatures. The values of the chemical constants calculated by the new formula agree, within the limits of experimental error, with those given by the formula $-C_0 = C - 1·5 \log M$, where C_0 is a universal constant, and M is the atomic weight. The values of C obtained from the vapour-pressure formula are given in the second column below; those from the above formula in the third column:

	C from vap. press.	C from formula.
Mercury	1·820 ± 0·032	1·845
Cadmium	1·65 ± 0·31	1·468
Zinc	1·23 ± 0·26	1·115

The value of C_0 is found to be $-1·622$. The latent heats of vaporisation are calculated from an expression previously used (*Phil. Mag.*, 1917, [vi], **33**, 193), and found to agree with the experimental values, as well as those calculated by the equation $\lambda = T_B 8·5 \log T_B$, due to Nernst. The value of Stefan's constant σ is calculated, and found to be $5·27 . 10^{-5}$ erg. cm.$^{-2}$ deg.$^{-4}$, which agrees with the value adopted by Planck, but is distinctly lower than the more recently determined values. J. R. P.

Significance of the Chemical Constant and its Relation to the Behaviour of Gases at Low Temperatures. F. A. LINDEMANN (*Phil. Mag.*, 1920, [vi], **39**, 21—25).—It is shown that the chemical constant has the dimensions of the logarithm of a pressure if the atomic heat of a monatomic gas becomes zero at the absolute zero. In this case it should be of the form $K + 3/2 . \log A + 5/2 . \log \theta$, where θ is a characteristic constant of the substance. If the atomic heat of a monatomic gas remains $5/2 . R$ down to the absolute zero, the chemical constant has the dimensions of a pressure divided by a temperature to the power 5/2, and is of the form $K + 3/2 . \log A$. Experimental determinations show that the latter form is true within the limits of error. It follows either that θ is very nearly equal to 1° for all substances, which seems improbable, or that the atomic heat remains constant down to the lowest temperatures. It is further shown that the chemical constant may be eliminated and the vapour pressure expressed in terms of the pressure of full radiation. It is therefore suggested that the

chemical constant may express the interaction of matter and full radiation rather than requiring that a gas can assume only a finite number of microphases, from the point of view of statistical mechanics, at a given temperature, pressure, and volume. If the valne of the chemical constant could, as suggested, be derived from the radiation pressure, the quantum assumption would be avoided in the case of gases, although it would be necessary for the deduction of the law of full radiation. J. R. P.

Latent Heat and Surface Energy. II. D. L. HAMMICK (*Phil. Mag.*, 1920, [vi], **39**, 32—46. Compare A., 1919, ii, 389).—On the assumption that van der Waals's constant, a, varies with the temperature, a relation is derived between the surface energy ρ, the molecular volume V, and a_T, namely, $a_T=6\rho V/d$, where d is the molecular diameter. This is valid at low temperatures only. By assuming that a_T diminishes linearly with the temperature to the critical value, a_c, latent heats are calculated by Bakker's formula, $\lambda=a_T(1/v_1-1/v_2)$, for several liquids. The results are in good agreement with experimental values. The ratio a_T/a_c is found to be the same for many liquids at the boiling point, and equal to 1·4. This leads to the value of Trouton's constant. The empirical relationship between latent heat and surface energy, due to Walden, and the Eötvös-Ramsay law, can also be deduced. J. R. P.

Heats of Fusion, Velocities of Crystallisation, and Chemical Affinities in Crystals. M. PADOA (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 239—243. Compare A., 1919, ii, 51, 96).—From the considerations previously developed, the conclusion is drawn that the affinity acting in the process of crystallisation should be expressed by, or at least included in, the heat of fusion of the compound, so that, under similar conditions as to molecular magnitude and structure, those compounds exhibiting the greatest velocities of crystallisation should also have the highest heats of fusion.

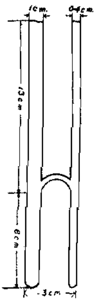
The melting points, heats of fnsion, and velocities of crystallisation are tabulated for a number of pairs of isomorphous organic compounds, such as naphthalene and dihydronaphthalene, benzene and *cyclo*hexane, etc. In each pair, the greater heat of fusion corresponds with the greater velocity of crystallisation characteristic of the compound containing double linkings. Further, unsaturated compounds, in general, melt at higher temperatures than the corresponding saturated compounds, this indicating the greater stability of the crystals of the former. As regards heats of fusion, the values for different series of compounds cannot be compared, the value for the saturated ethyl succinate, for instance, exceeding that for benzene; thus, the heat of fusion may be the resultant of various thermal effects, and not merely the effect of the affinity inherent to the union of the molecules in the crystal, in the same way as the heat of solution represents the algebraic sum of the various heats of ionisation, hydration, etc.

With a compound containing a triple linking, such as tolane, the velocity of crystallisation is less than that for the corresponding

isomorphous compound with a double linking (stilbene), and approaches that for the corresponding compound with a single linking (dibenzyl). The parallelism between velocity of crystallisation and heat of fusion is maintained also in this case; the melting points of compounds with triple linkings are likewise lower than those of the compounds with double linkings.

The high velocities of crystallisation shown by compounds with double linkings are explainable on the assumption that change of form on crystallisation is unnecessary with these compounds, which in the liquid state are wholly of the fumaric or wholly of the maleic type, and with the help of the latent valencies crystallise with great rapidity; on the other hand, the compounds with single or triple linkings undergo, in part at least, a preliminary transposition, which results in retardation of the crystallisation. As an instance of the influence of the molecular configuration, it may be noted that the velocity of crystallisation of dibenzyl, with which equilibrium, between the *cis*- and *trans*-forms is possible in solution, is 580 mm. per minute, whereas that of dihydrophenanthrene, which differs from dibenzyl only in the closure of the third ring, and with which no equilibrium between isomeric forms is possible, is 1200 mm. per minute.

It may be, however, that the results obtained with compounds containing the three different linkings are to be explained by the assumption tbat the latent valencies of the triple linking exert no action in the formation of crystals. Thomsen's thermochemical calculations ("Thermochemische Untersuchungen," 1906, 310) show that the thermal value of a simple linking in the lower members of the paraffin series is 14·71 cal., whereas that of the double linking in the corresponding olefines is 13·27 cal., and that of the triple linking in acetylene, etc., approaches zero. T. H. P.



Apparatus for Determining the Melting Point of Very Hygroscopic Substances. H. J. Backer (*Chem. Weekblad*, 1919, **16**, 1564—1565).—The apparatus consists of a narrow, thin-walled glass tube, into which the material under examination is placed, the tube being then drawn out and sealed. It communicates bv means of a small, curved, lateral branch with a wider tube, in which is placed about 2 c.c. of phosphoric oxide, after which this tube is drawn out into a capillary, exhausted by means of a water-pnmp, and sealed. The material is thus contained in a vacuum desiccator during the determination of its melting point. W. J. W.

Freezing-point Lowerings in Mixtures of Two Electrolytes. K. G. Dernby (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 18, 1—10).—The depression of the freezing point has been determined for aqueous solutions of mixtures of two electrolytes. The following pairs were examined: hydrochloric acid and the

chlorides of sodium, potassium, and magnesium respectively, potassium and magnesium chloride, nitric acid with potassium and magnesium nitrates respectively. The concentrations examined varied between 0*N* and 0·8*N*. It is shown that the freezing-point lowerings of mixtures of electrolytes with a common negative ion are always greater than the sum of the individual lowerings. For mixtures of binary electrolytes, such as KCl,HCl, NaCl,HCl, KNO_3,HNO_3, the lowering of the freezing point is approximately proportional to the concentration of the salt and of the acid. For mixtures of a ternary electrolyte and a binary electrolyte, such as $MgCl_2$,HCl, $MgCl_2$,KCl, and $Mg(NO_3)_2$,HNO_3, the lowering of the freezing point increases faster than the concentration. Mixtures of magnesium chloride and hydrochloric acid lower the freezing point more than mixtures of potassium chloride and magnesium chloride of the same concentration. J. F. S.

Calculation of the Neutral Salt Action from the Depression of the Freezing Point of Aqueous Solutions. SVANTE ARRHENIUS and ERIK ANDERSSON (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 25, 1—9).—A theoretical paper in which, on the basis of the Arrhenius hypothesis of the mechanism of neutral salt action, an attempt is made to calculate the neutral salt action from freezing-point depressions. The osmotic pressure of a solution is strongly influenced by other substances, particularly salts; this is also true of the osmotic pressure of hydrogen ions. Since the velocity of reaction is proportional to the osmotic pressure of the surrounding substance (sucrose or ethyl acetate), and, further, the osmotic pressure of the catalyst (hydrogen ions) increases proportionally, the neutral salt action can be calculated as soon as the corresponding changes of the two osmotic pressures are known. These for the case under investigation are known from the freezing-point measurements of Dernby (preceding abstract) and from the hydrogen-ion activity determinations of Harned (A., 1916, i, 8). The calculation shows that the method is one capable of furnishing the desired result. J. F. S.

Simplification of the Inverse-rate Method for Thermal Analysis. P. D. MERICA (*Bull. Bureau Standards*, 1919, *No.* 336, 101—104).—In plotting and recording cooling curves, the author recommends the following method, using a thermocouple, a direct-reading potentiometer and galvanometer, and two stop-watches. The watches are mounted in a single frame and held in one hand; the potentiometer is set at the desired point. When the time-temperature readings are being made, the stem of both watches is pressed at the moment the galvanometer reaches the zero, thus stopping one watch and so recording the time interval, and starting the other watch on the next interval, which is recorded in the same way. This method saves the time necessary in plotting and reading chronograph records, and does away with the use of expensive chronographs. Specimen curves for the cooling of iron made by this method are given in the paper. J. F. S.

Exact Formula for the Saturation Tension of Water Vapour between 0° and 50°. PAUL SCHREIBER (*Physikal. Zeitsch.*, 1919, **20**, 521—523).—The author gives the following formulæ for calculating the saturation tension of water vapour at temperatures between 0° and 50°: $\log s = \log s_1 + \log f(T)$, in which $\log s_1 = p + q \log T$ and $\log f(T)$ is a correcting factor, s is the corrected saturation tension. The values calculated by this equation are practically identical with the values given in the international meteorological tables. The values $\log s_1 = -7{\cdot}0814 + 17{\cdot}8 \log (10^{-2}T)$, $\log f(T) = 0{\cdot}0115 - 0{\cdot}0000494(T-298)^2$ and

$$\log s = -7{\cdot}0699 + 17{\cdot}8 \log (10^{-2}T) - 0{\cdot}0000494(T-298)^2$$

are used in the calculations. J. F. S.

Boiling Point of Liquids. F. P. SOEBEL (*Science*, 1919, **50**, 49—50).—Assuming that at the b. p. the energy of vibration of the individual molecules of a liquid and of its vapour must be equal, the author deduces the equation $T_x = mp_xv_x/1{\cdot}49$ for a pure liquid, where m is the molecular weight and p_x and v_x the pressure and the volume of the vapour at the absolute b. p., T_x. For ordinary liquids containing impurities, the equation becomes $T_x = (p_xv_x - C)m/1{\cdot}49$, where C is a constant characteristic of each liquid. In the case of water ($m = 18$; $C = 8{\cdot}7$), the calculated values of T_x at 273°, 313°, and 473° (abs.) are 270°, 313·3°, and 473·5° respectively. Similar agreement is found in the case of other liquids in which association does not occur. CHEMICAL ABSTRACTS.

Vapour Pressure and Free Energies of the Hydrogen Haloids in Aqueous Solution. The Free Energy of Formation of Hydrogen Chloride. STUART J. BATES and H. DARWIN KIRSCHMAN (*J. Amer. Chem. Soc.*, 1919, **41**, 1991—2001).—Determinations have been made of the vapour pressures of hydrogen chloride, hydrogen bromide, and hydrogen iodide above their aqueous solutions between the concentrations 3·2 and 10·0*N*, 5·8 and 11·0*N*, and 6·0 and 9·7*N*, respectively, at 25°, and of hydrogen chloride between 5·5 and 9·2*N* at 30°. By the method employed, which consisted in determining the hydrogen haloid contained in a given quantity of air or nitrogen in equilibrium with its solution, and comparing this with the amount of aqueous vapour which the same air contained when in equilibrium with pure water at the same temperature, partial pressures as small as 0·001 mm. were determined with an accuracy of a few per cent. The vapour-pressure measurements of hydrochloric acid solutions between 3·2*N* and 7·15*N* are in good agreement with the *E.M.F.* data for hydrochloric acid concentration cells. The free energy of formation of hydrogen chloride at 25° is −22,700 cal. The free energies of formation of the halogen acids at various concentrations, 0·1—11·0 mols. per litre, in aqueous solution are given in a table in the paper.

J. F. S.

Constant Temperature Still-head for Light Oil Fractionation. FREDERICK M. WASHBURN (*J. Ind. Eng. Chem.*, 1920, **12**, 73—77).—The apparatus described consists of two essential

parts, namely, a Hempel column and a constant temperature still-head of the type suggested by F. A. Brown (T., 1880, **37**, 49). This still-head is a spiral of about 6 inches diameter made from 12 feet of $\frac{3}{8}$ inch iron tube; it is surrounded by an oil-bath, which is provided with a stirrer and maintained at the required temperature by a coil of resistance wire, thermo-regulator, relay, etc. The lower end of the spiral is connected with the side-tube of the Hempel column, whilst the upper end is fitted with a thermometer pocket and a side-tube leading to an ordinary condenser. W. P. S.

Heat of Formation Calculated from the Wave-length of Absorption Bands. A. L. Bernouilli (*Helv. Chim. Acta*, 1919, **2**, 720—728).—The author has deduced an expression, whereby from the absorption bands corresponding with characteristic ultra-violet electron vibrations the heat of formation of a compound from its elements may be calculated. This expression for a binary compound has the form $Q = 0{\cdot}01128[(\sqrt{\Theta_1/\alpha v_1^{2/3}} - \sqrt{\Theta_2/\beta v_2^{2/3}}) - \sqrt{\Theta'/(\alpha+\beta-\delta)v'^{2/3}}]$, in which Q is the heat of formation, v_1, v_2, and v' the atomic volumes of the constituent elements and the molecular volume of the compound respectively; Θ_1, Θ_2, and Θ' are the melting points, in absolute degrees, of the elements and the compound respectively, α and β are the electron numbers or valencies of the elements, and δ is the number of charges given up in the formation of the molecule. This formula is tested in the case of a number of binary compounds, and the results compared with the experimental values. The two sets of results are remarkably close; for example, carbon dioxide, calc. 108·3, obs. 106·0; silver chloride, calc. 29·05, obs. 29·0. J. F. S.

Heat of Reaction of Ammonia Oxidation. Guy B. Taylor (*J. Ind. Eng. Chem.*, 1919, **11**, 1121—1123).—The temperature most favourable to the catalytic oxidation of ammonia by means of air is 800°. In order to determine the amount of external energy required to maintain the catalyst at the optimum temperature a formula has been based on the equations:

(1) $4NH_3 + 5O_2 = 4NO + 6H_2O + 214200$ cal.

(2) $4NH_3 + 3O_2 = 2N_2 + 6H_2O + 300600$ cal.

The temperature rise is expressed by the formula $t = Q/C$, where Q represents the heat of reaction in calories, and C the specific heat of the products of the reaction. From 0° to 800° water-vapour is the only gaseous product with an appreciable temperature-coefficient, and this may be taken as 8·34. In the following formula, $t^\circ = (75150x - 21600y)/(7{\cdot}08 + 3{\cdot}41x - 0{\cdot}25y + 8{\cdot}34V/B - V)$, V represents the partial pressure of water-vapour, B the total pressure of the air–ammonia–water vapour mixture, x the molecular fraction of ammonia in the mixture, and y the molecular fraction of nitric oxide produced in the oxidation. For maintaining the catalyst at the right temperature, pre-heating the mixture, electric heating, or enriching the current of ammonia and air with oxygen have been shown to give equally satisfactory results. C. A. M.

Critical Densities of Hydrogen, Helium, and Neon. J. J. VAN LAAR (*Chem. Weekblad*, 1919, **16**, 1557—1564).—In the cases of hydrogen and helium the extrapolated values for D_c obtained from the curve $\frac{1}{2}(D_1+D_2)=f(T)$ are found to be too high. Thus the figure 0·0310 so obtained for hydrogen would correspond to $\gamma=0{\cdot}46$, which is an impossible value. The author calculates that for hydrogen $D_c=0{\cdot}0287$, and for helium $D_c=0{\cdot}0598$ instead of 0·066 as given by the curve.

In the case of neon there is agreement between the extrapolated value and the calculated figure, D_c being 0·456. W. J. W.

The "Density Numbers" of Groshans. W. P. JORISSEN (*Chem. Weekblad*, 1917, **14**, 1066—1071).—The volume in c.c. of 1 gram of a vaporised substance at the boiling point is given by the expression $82T_{b.p.}/M$, where M is the molecular weight. Elimination of $T_{b.p.}$ between this expression and the boiling point formula of Groshans, $T_{b.p.} = 27{\cdot}8M\sqrt{x/n}$, gives the vapour volume in c.c. of 1 gram $2280\sqrt{x/n}$. x is a constant for the class of substances considered, and n is the sum of the density numbers of the elements involved (*Ann. Phys. Chem.*, 1849, **78**, 116). For the elements carbon, hydrogen, and oxygen the density numbers are unity, and n is therefore the number of atoms in the molecule. For other elements n is greater than unity. For unassociated liquids the expansion in the transition from liquid to vapour is $570\sqrt{x}$. By comparing this formula with the expansion determined experimentally by Masson (A., 1891, 379) for methyl, ethyl, propyl, phenyl, butyl, and amyl chlorides, x is determined for each, and the density number for chlorine is determined from the boiling-point formula. The values found range from 3·40 to 4·44. The value given by Groshans is 4. W. S. M.

Determination of Avogadro's Normal Volume V_A and of the Atomic Weights of Hydrogen, Helium, and Argon. J. J. VAN LAAR (*Chem. Weekblad*, 1919, **16**, 1243—1250).—A continuation of a previous communication (A., 1919, ii, 461).

The most probable value of V_A is considered to be 22415^3 c.c. The atomic weights of hydrogen, helium, and argon are stated to be 1·007697 (=1·00770), 3·9998 (=4·000), and 39·95 respectively. W. J. W.

Molecular Attraction. III. The Characteristic Equation. K. K. JÄRVINEN (*Ann. Acad. Sci. Fennicae*, 1919, [*A*], **12**, Reprint 44 pp.).—A continuation of the theoretical discussion on molecular attraction (compare A., 1913, ii, 293; A., 1915, ii, 251). The internal pressure, p_a, is calculated by the equation $p=RT/V.f-p_a$, on the basis of the law of molecular attraction $F=km^2/r^5$. It is found that $p_a=a/v^{4/3}$ for monatomic substances, and $p_a=a/\{v^{2/3}(v^{1/3}-0{\cdot}242b^{1/3})^5\}$ for polyatomic substances, where a and b are the constants of van der Waals's equation. It is thus much smaller than that calculated from the latter equation. The critical pressure, $p_k=RT/V.f$, is also calculated, and thence a table of values of f

deduced, which may be used to find the deviations from the ideal state. Values of f are also calculated from the equations $f = p - p_a / RT \cdot v$ and $f = dp/dt \cdot v/R$, the latter obtained by differentiation of the characteristic equation. These agree approximately with the theoretical values. The differences are taken to mean that the theory is yet incomplete. It is also found that b decreases with temperature, but this need not in reality be the case. The pressure, the critical data, and the values of v_k/b_0, RT/pv_k, $dp/dt \cdot v/R$, and $dp/dt \cdot T/p$, may be obtained with fair approximation. Only approximate accuracy is claimed. J. R. P.

Effects of Acids and Bases on the Surface Energy Relations of ββ′-Dichloroethyl Sulphide (Mustard Gas). William D. Harkins and D. T. Ewing (*J. Amer. Chem. Soc.*, 1919, **41**, 1977—1980).—The surface tension between ββ′-dichloroethyl sulphide and a number of liquids has been determined with the object of finding a suitable emulsifying agent for the preparation of aqueous emulsions of this substance. The following values of the surface tension in dynes per cm. have been found between ββ′-dichloroethyl sulphide and the liquids named: water, 28·36; 0·1*N*-hydrochloric acid, 28·90; 0·1*N*-sodium hydroxide, 12·78; 0·1*N*-sodium carbonate, 18·82; 1% solution of turkey-red oil, 14·47; 1% solution of turkey-red oil in 0·1*N*-sodium carbonate, 8·35; 1% Twitchell's solution, 12·32; 1% Twitchell's solution in 0·1*N*-sodium carbonate, 12·89; 1% maize oil solution, 12·94; and 1% maize oil in 0·1*N*-sodium carbonate, 10·91. The surface tension of several organic liquids has also been measured: αα-diphenylpropane, 20°, 37·15, 25°, 36·64; αα-diphenylethane, 20°, 37·67, 25°, 37·20; diphenylmethane, 20°, 37·56; ditolylmethane, 20°, 35·51, 25°, 34·80; propylbenzene, 20°, 32·22, 25°, 31·30. All determinations were made by the drop-weight method. J. F. S.

Viscosity of Pure Liquids. Svante Arrhenius (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 20, 1—40).—A theoretical paper, in which a large volume of work on the viscosity of liquids is discussed and correlated. It is shown that the ratio $\eta_b \times 10^5 : \sqrt{s}$ is approximately constant for non-associated organic liquids. The symbols have the significance, η_b is the viscosity of a liquid at the boiling point and s is the density, and the constant varies between 230 and 320. The constant is not obtained in the case of a few liquids, which are characterised by the fact that the expression $K_1 = T^2(d \log \eta / v^{\frac{1}{3}})/dt$ does not show a minimum below the boiling point. These liquids are ethylene, propylene, and *iso*butylene bromides, benzene, and carbon tetrachloride. The presence of negative atoms, such as the halogens, sulphur, or oxygen, increases the value of the ratio $\eta_b : \sqrt{s}$. The influence of pressure on the viscosity is nearly represented by a linear equation $\log \eta_p = \log \eta_0 + l(p - p_0)$, where η_0 is the viscosity at the external pressure zero (practically atmospheric pressure), p is the total pressure (external and internal) calculated according to van der Waals's

theory, and p_0 the internal pressure at zero external pressure. The influence of temperature on viscosity may, for non-associated liquids, be expressed by the formula $d \log \eta \cdot v^{\frac{1}{2}}/dt = K_1/T^2$. K_1 is nearly proportional to the absolute boiling point T_b, so that $K_1 : T_b$, if ordinary logarithms are used for calculating K_1, does not change for normal organic liquids between greater limits than 1—1·2. Benzene and the liquids named above are exceptions. For associated liquids the ratio $K_1 : T_b$ possesses higher values, between 1·25 and 4·32. There is a pronounced parallelism between the values of the ratios $\eta_b : \sqrt{s}$ and $K_1 : T_b$. In an homologous series, $K_1 : T_b$ generally increases with the boiling point. There is a great analogy between the effect of temperature on the vapour pressure and on the product of the viscosity and the specific volume. J. F. S.

Investigations concerning the Viscosity of Binary Liquid Mixtures. HANS EGNÉR (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 22, 1—13).—A theoretical paper in which a large number of viscosity determinations of various authors are collected and examined in connexion with the modified logarithmic formula of Arrhenius, $\log \eta = n_1 \log \eta_1 + n_2 \log \eta_2$, where η_1 and η_2 are the viscosities of the components of the mixtures, and n_1 and n_2 the molecular concentrations. It is shown that this formula represents the variation of the viscosity in binary liquid mixtures more exactly than any other formula. J. F. S.

Theoretical Significance of Viscosity Measurements of Colloidal Solutions. SVANTE ARRHENIUS (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, **3**, No. 21, 1—22).—A theoretical paper in which a large number of viscosity determinations of colloidal solutions are discussed. It is shown that Einstein's viscosity formula is fully established by Bancelin's results (A., 1911, ii, 586, 1067) as soon as the logarithmic formula

$$\log \eta - \log \eta_0 = \theta \phi$$

is employed. The proposed extension of Einstein's formula put forward by Smoluchowski is not confirmed by Oden's measurements on colloidal sulphur (A., 1913, ii, 485). J. F. S.

Viscosimeter for Measuring Viscosities and Fluidities. GEORGES BAUME and HENRI VIGNERON (*Ann. Chim. anal.*, 1919, [ii], **1**, 379—383).—The viscosimeter tube consists of a capillary provided with a bulb at its upper end and a short length of wide tube at its lower end; this tube is fixed vertically by means of a cork in a test-tube containing 20 c.c. of the oil under examination, the lower end of the tube being immersed in the oil up to a mark just below the capillary. A thermometer passes through a T-piece carried by the cork, the bulb of the thermometer dipping into the oil. The test-tube is inserted in a boiling bulb provided with a reflux apparatus. This boiling bulb may contain ether, acetone, benzene, or water, according to the temperature at which the viscosity is to be determined; when the required temperature has

been reached, the oil is forced upwards into the viscosimeter tube by a pressure ball attached to a branch of the T-piece; the pressure is then released, and the time taken for the level of the oil to fall from a mark just above the bulb (on the viscosimeter tube) to one just below it is noted. W. P. S.

Emulsification by Adsorption at an Oil-Water Interface. S. E. SHEPPARD (*J. Physical Chem.*, 1919, **23**, 634—639).—Emulsions of nitrobenzene in sulphuric acid and hydrochloric acid may be readily prepared by making the acid of the same density as the nitrobenzene. Similar moderately stable emulsions were prepared by saturating the acid (sulphuric) with lead sulphate or calcium sulphate, or hydrochloric acid with sodium chloride or lead chloride, in both cases the acid being of the same density as the nitrobenzene. It therefore appears that, in accordance with Bancroft's general theory of peptisation, adsorption at a liquid–liquid interface is capable of effecting emulsification. The systems thus produced, on ageing, pass into a condition approaching Pickering's emulsions, but with a great diminution of the dispersity.

J. F. S.

Nature of Osmotic Pressure. MITSUJI KOSAKAI (*Proc. Soc. Expt. Biol. Med.*, 1919, **16**, 118—119).—The hæmolytic effects of formaldehyde and carbamide were found to be like that of boric acid, the result of osmotic pressure. The rates of diffusion of boric acid, formaldehyde, and carbamide are 90 sec., 30 sec., and less than 5 sec. respectively. These differences correspond with the differences in the hæmolytic action of the three substances, and confirm the view that osmotic pressure is not a direct property of a solute, but is merely water pressure developed by the process of diffusion.

CHEMICAL ABSTRACTS.

Osmotic Pressure. II. The Nature of Osmotic Pressure. MITSUJI KOSAKAI (*J. Immunology*, 1919, **4**, 49—65).—The same degree of osmotic hæmolysis is not produced by identical concentrations of boric acid, formaldehyde, and carbamide, or by a corresponding lowering in the medium of suspension of the treated corpuscles. As the treating concentration of the three hæmolytic substances is correspondingly diminished, the ratio between that concentration and the final concentration, in the hæmolytic experiment, increases disproportionately with the different substances. The osmotic hæmolysis of corpuscles which have been treated with the three hæmolytic substances in the same osmotic concentration is not inhibited by identical concentrations of sodium chloride or of the hæmolytic substances themselves. All these facts contradict the assumption that osmotic pressure is exerted directly by the solute. Osmotic pressure is not a direct property of a solute, but is solely the pressure exerted by water which has passed, by the unexplained process of diffusion, through a semipermeable membrane to the side of the higher osmotic concentration.

CHEMICAL ABSTRACTS.

Osmotic Pressure of an Electrolyte. OSKAR KLEIN (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 6, 1—9).—A mathematical paper in which an expression is deduced showing the connexion between osmotic pressure, concentration, temperature, and dielectric constant. The reasoning is based on thermodynamical and mechanical (kinetic) principles, and is simpler than that used by Milner (A., 1913, ii, 481) in a similar problem. T. S. P.

The Diffusion of Electrolytes into Jellies. II. The Dependence of the Diffusion on the Mobility of the Ions and the Hydration and Polymerisation of the Molecules. OTTO VON FÜRTH and FRANZ BUBANOVIĆ (*Biochem. Zeitsch.*, 1918, **92**, 139—170. Compare A., 1919, ii, 13).—Diffusion in jellies differs in most cases from free diffusion in aqueous solution, and is dependent on the character of the jelly. The velocity with which acids, bases, and polymerised salts penetrate jellies is smaller than would be expected from the mobility of their ions. Weakly hydrated salts show normal diffusion (diffusion similar to that in aqueous solution) in jellies. Strongly hydrated salts, on the other hand, contrary to their behaviour in aqueous solution, diffuse relatively faster than in the previous case, so that their diffusion velocity approximates to the theoretical value obtained from the mobility of the ions. S. S. Z.

Influence of the Concentration of Electrolytes on the Electrification and the Rate of Diffusion of Water through Collodion Membranes. JACQUES LOEB (*J. Gen. Physiol.*, 1919, **20**, 173—199).—When an aqueous solution is separated from pure water by a collodion membrane, the initial rate of diffusion of water into the solution is influenced in an entirely different way by solutions of electrolytes and of non-electrolytes. The latter influence the rate of diffusion in direct proportion to their concentration, and this effect is termed the gas-pressure effect. Solutions of electrolytes show the gas-pressure effect also, but it commences at a somewhat higher concentration than in the previous case. If the concentration of the electrolyte is below that at which the gas-pressure effect is observed, the solutions have a specific influence on the initial rate of diffusion, which is not found in the case of the solutions of non-electrolytes, and is due to the diffusion of the water in an electrified condition, the sign of the charge depending on the nature of the electrolyte in solution, according to the theory which has been advanced by the author (A., 1919, ii, 497). In these lower concentrations, the curves representing the influence of the concentration of the electrolyte on the initial rate of diffusion of water into the solution show that, within a range of concentrations between $M/256$ and $M/16$ or more (according to the nature of the electrolyte), the reverse of what should be expected on the basis of van't Hoff's law is noticed, namely, that the attraction of a solution of an electrolyte for water diminishes with an increase in concentration. Whilst no definite assumption concerning the

origin of the electrification of water and the mechanism by which the ions influence the rate of diffusion of water particles through collodion membranes is made, it is suggested that in the lowest concentrations, attraction of the electrified water particles by the ions with the opposite charge prevails over the repulsion of the water particles by ions with the same sign of charge, whilst beyond a certain critical concentration the repelling action of the ion with the same charge as that of the water particles on the latter increases more rapidly with increasing concentration of the solute than the attractive action of the ion with the opposite charge.

It is shown that negative osmosis is due to the repulsion of the electrified particles of water by the ion with the same charge as that borne by the water. J. C. D.

The Effect of Strain on Solubility. J. C. HOSTETTER (*Science*, 1919, **50**, 25).—It is possible that fluctuating temperature and, perhaps, some indirect effects brought about by pressure may account for the solidification of crystals compressed in contact with their solution by loosely fitting pistons, as found by James Thomson, Le Chatelier, and Spring, without the necessity of postulating large increases in solubility due to non-uniform pressure. In preliminary experiments, individual crystals were subjected to stress at constant temperature by direct loading, and the effect on the concentration of the surrounding solution was studied by measuring the electrical conductivity. No change in concentration was found. The test was sufficiently sensitive to indicate that the effect of non-uniform pressure is much less than that produced by the same pressure acting uniformly. However, in another series of experiments, in which an unloaded crystal was placed alongside a loaded crystal, the former grew at the expense of the latter, showing that a very slight increase of solubility was produced by the stress. The method of loading the crystals has a large influence on the effects found, thus indicating the importance of the stress distribution. The experiments of Becker and Day on the linear force of growing crystals are cited as indicating the stability of a crystal in its solution, even when subjected to pressure. In their experiments, loaded crystals were found to lift the load during growth, although the pressures on the supporting edges of the crystals were finally of the order of magnitude of the crushing strength of the crystal. The evidence so far obtained indicates that the effect of strain on solubility is a second-order effect.

CHEMICAL ABSTRACTS.

Influence of Electrolytes on Solubility. EBBE LINDE (*Arkiv. Kem. Min. Geol.*, 1917, **6**, No. 20, 1—17).—The solubility of ethyl ether and ethyl acetoacetate has been determined in water and in solutions of certain electrolytes. In the case of ethyl ether, it is found that 7·88 grams dissolve in 100 c.c. of water at 18°. The influence of mixtures of two electrolytes on the solubility of ether in water is determined for the pairs of electrolytes, sodium

sulphate–sulphuric acid, sodium sulphate–sodium hydroxide, and sodium chloride–sodium acetate. In the first two pairs, the total electrolyte concentration was 0·5*N*, and in the last pair *N*. The concentrations of the two electrolytes were varied within these limits. For the pair of electrolytes, sodium sulphate–sulphuric acid, it is shown that the solubility is 5·52 grams per 100 c.c. of 0·5*N*-sodium sulphate, and rises regularly with decreasing sodium sulphate concentration and increasing sulphuric acid concentration to 7·72 grams per 100 c.c. of 0·5*N*-sulphuric acid. In 0·5*N*-mixtures of sodium sulphate and sodium hydroxide, the solubility is constant, 5·53 grams per 100 c.c. of solution, whilst in the case of sodium chloride and sodium acetate the solubility is 4·62 grams in 100 c.c. of *N*-sodium chloride, and falls regularly to 3·44 grams in 100 c.c. of *N*-sodium acetate. The electrolytes are seen, therefore, to have an additive effect. The solubility is also determined in solutions of sodium acetate and sodium chloride of varying concentration, and in both cases shown to increase steadily with increasing dilution, but in neither case is the depression of the solubility in keeping with Steiner's expression. Both sets of solubility values are fairly in keeping with the expression of Hoffmann and Langbeck (A., 1905, ii, 374). The solubility of ethyl acetoacetate has been determined in water, and solutions of sodium chloride and sodium nitrate of various concentrations at 16—16·5°. It is shown that 100 c.c. of water dissolve 12·5 grams of ethyl acetoacetate at 16—16·5°. In *N*-sodium chloride, 8·4 grams dissolve in 100 c.c., and this value increases with decreasing concentration of sodium chloride, but the solubility change is in keeping with neither of the above expressions. In sodium nitrate solution, 11·4 grams of ethyl acetoacetate dissolve in 100 c.c. of *N*-sodium nitrate, and the solubility increases in accordance with both the above-named expressions on decreasing the nitrate concentration. The addition of alcohol to solutions of sodium chloride and nitrate increases the solubility of ethyl acetoacetate in these solvents. J. F. S.

Contrasting Effects of Chlorides and Sulphates on the Hydrogen-ion Concentration of Acid Solutions. ARTHUR W. THOMAS and MABEL E. BALDWIN (*J. Amer. Chem. Soc.*, 1919, **41**, 1981—1990).—The hydrogen-ion concentration of a chrome tanning liquor has been determined in the presence of various concentrations of sodium chloride, ammonium chloride, sodium sulphate, ammonium sulphate, and magnesium sulphate. The effect of the addition of chlorides is to increase the hydrogen-ion concentration, whilst that of sulphates is to decrease it, although, on keeping, the concentration increases somewhat. Similar experiments were carried out with pure chrominm sulphate solution, chromium chloride solution, sulphuric acid (0·0005*N*), hydrochloric acid (0·004*N*), sulphuric acid (0·1*N*), and hydrochloric acid (0·1*N*), using a number of chlorides and sulphates. In every case, the chlorides are found to increase the hydrogen-ion concentration, and

the sulphates to reduce it. The power of increasing the hydrogen-ion concentration follows the order

$$MgCl_2 > BaCl_2 > LiCl, > NaCl > NH_4Cl = KCl.$$

J. F. S.

Degree of Ionisation of Very Dilute Electrolytes. GILBERT N. LEWIS and GEORGE A. LINHART (*J. Amer. Chem. Soc.*, 1919, **41**, 1951—1960).—A theoretical paper in which the authors deduce a general equation for the freezing-point lowering of dilute strong electrolytes. This equation has the form $n\lambda - \theta/c = \beta c^{\alpha}$, in which n is the number of dissociated parts, λ the degree of dissociation, θ the lowering of the freezing point, c the concentration, and β and α characteristic constants. The calculation and observed values of θ for fourteen salts at a series of concentrations are compared and shown to be in good agreement. The thermodynamic degree of dissociation is calculated for the same salts over a range of concentration 10^{-1}—$10^{-8}N$. The constants α and β of the above equation can be obtained from freezing-point determinations. The calculated degree of dissociation diverges extraordinarily from the value obtained by the usual method. J. F. S.

The Influence of the Dielectric Constant of the Solvent and of the Electric Energy of the Ions on Electrolytic Dissociation. MARIO BASTO WAGNER (*Anal. Fis. Quim.*, 1919, **16**, 229—257).—A purely mathematical paper. W. S. M.

Mechanism of Electrolytic Dissociation. B. CABRERA (*Anal. Fis. Quim.*, 1918, **16**, 186—225).—A mathematical paper developing the theory that the ions resulting from the solution of a crystalline snbstance are already present as such in the crystal, the formation of neutral molecules being thus subsequent to the act of solution or fusion. W. S. M.

Atomic Constitution of a Crystal Surface. E. MADELUNG (*Physikal. Zeitsch.*, 1919, **20**, 494—496).—A mathematical paper in which the author considers the condition of the surface layer of molecules in crystals of the sodium chloride type. It is shown that in crystals of the regular type, consisting of binary compounds, the atoms of one kind on the surface are displaced in directions at right angles to the surface with respect to the atoms of the other kind. The displacement decreases in the body of the crystal according to a simple exponential equation. It is also shown that, since the atoms of electrolytes carry electric charges, an electric double layer must, in consequence of the displacement, surround the crystal surface. J. F. S.

A New Method of Electrical Synthesis of Colloids. THE. SVEDBERG (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 10, 1—18).—The author has prepared gold and silver sols of high dis-

persion by a modified method. The apparatus consists of a quartz tube in which a small hole about 1 mm. diameter is bored. The metal electrodes, gold or silver, pass down this tube, and are so placed that the arc may be formed opposite the hole. The quartz tube is so arranged that a current of nitrogen passes through it both from the top and the bottom. The quartz tube is placed in an outer glass jacket containing about 30 c.c. of the dispersion medium (alcohol), and this jacket is surrounded by a further jacket containing a cooling agent (ice and salt or solid carbon dioxide and alcohol). An electromagnet is placed with its poles on either side of the small hole in the quartz tube. The current (1 amp. 220 volts) is switched on, and an arc of the usual type appears for about a second, then, owing to a melting of the lower electrode (anode), the quartz tube becomes somewhat stopped up, and so the electrode is protected from the dispersion medium; the arc becomes a sharp-pointed flame, and this is drawn through the hole in the tube by the action of the magnet. Metallic clouds appear and are absorbed by the dispersion medium. The appearance of the arc has been examined spectrographically in both conditions and the differences noted. The author holds that the condensation of metal vapour is the cause of the sol formation. Other forms of apparatus are described in the paper. J. F. S.

Colloid Metal Reactions. Spectrum Analysis and Blood Colouring Matter. EDUARD RICHTER (*Kolloid. Zeitsch.*, 1919, **25**, 208—211).—A number of colloid reactions between 1% gold chloride solution and 1:1000 solutions of adrenaline, alloxan, tannic acid, and *p*-phenylenedimethyldiamine are described. In each case, colloidal gold is produced, but of different degrees of dispersity. From the experiments, it is deduced that certain diamines possess a particularly powerful reducing action, and are probably to be classified with the reducing substances of the amino-group which occur in the animal organism. Certain hydroxy-substances also show a similar reducing action. J. F. S.

Colour of Colloids. IX. WILDER D. BANCROFT (*J. Physical Chem.*, 1919, **23**, 554—571. Compare A., 1919, ii, 500).—A continuation of the previous discussion. It is shown that with very small particles, the light which is ordinarily reflected selectively is transmitted by resonance, whilst the light which is ordinarily transmitted is scattered. Massive gold is red by multiple reflection, and thin films are green by transmitted light. Very small particles reflect green and transmit red light. Massive gold reflects yellow when compact, and brown to black when porous. Particles which do not resonate are yellow or brown by reflected light and transmit blue light. Silver is yellow by multiple reflection, and thin films are blue to green by transmitted light. Very small particles reflect blue and transmit yellow. Particles which do not resonate transmit blue light and reflect red. Colloidal indigo solutions transmit red light, and the surface colour of indigo is red. Sodium fog scatters

blue light and transmits the yellow, which the vapour absorbs. Iodine fog scatters red light. J. F. S.

Colours of Colloids. X. Wilder D. Bancroft (*J. Physical Chem.*, 1919, **23**, 603—633. Compare A., 1919, ii, 500).—A continuation of the previous discussion. In the present paper the colours of glasses and glazes are considered. It is shown that in glasses and glazes, gold, silver, copper, platinum, iridium oxide, selenium, tellurium, sulphur, lead antimonate, carbon, magnetite, ferric oxide, stannic oxide, zirconium oxide, arsenious oxide, titanium oxide, and calcium phosphate occur usually as a second phase. Chromium occurs in some form as a second phase in chrome Aventurine glass and copper in Egyptian blue. Some glasses coloured by iron, chromium, manganese, and cobalt are optically empty. In enamels the substance causing the colour is probably chiefly adsorbed by the material causing the opacity. J. F. S.

Colours of Colloids. XI. Wilder D. Bancroft (*J. Physical Chem.*, 1919, **23**, 640—644. Compare preceding abstract).—A continuation of the previous discussion. In the present paper the colours of gem stones are considered. J. F. S.

Coagulation. Arne Westgren (*Arkiv. Kem. Min. Geol.*, 1918, **7**, No. 6, 1—30).—The coagulation of gold sols has been examined with the object of ascertaining the influence of the size of the colloid particles, the nature of the coagulating ions, and the temperature on the velocity of the slow coagulation. Forty c.c. of the sol were mixed with 10 c.c. of an electrolyte, and after definite intervals of time had elapsed 5 c.c. of the mixture were withdrawn and run into 25 c.c. of 0·5% gelatin solution and the particle concentration determined. Using sols with particles of radius 120 $\mu\mu$, 77 $\mu\mu$, and 49 $\mu\mu$ respectively, it is shown that the velocity of coagulation is independent of the size of the particles. Using the following electrolytes to coagulate the sols (hydrochloric acid, sodium, lithium, potassium and rubidium chlorides, sodium hydroxide, and sodium iodate), it is shown that the ionic conductivities of the ions are determinative of the coagulating power. Thus hydrochloric acid, the cation of which has the greatest ionic conductivity, is the most active coagulator of all the chlorides, whereas lithium chloride with its slow-moving cation is the least active. Potassium chloride and rubidium chloride, which have cations of about the same ionic conductivity, have about the same coagulating power. Since gold sols are negative colloids, it follows that when they are coagulated by cations the anions must exercise a stabilising influence, and this is shown in the coagulation by sodium derivatives, for sodium hydroxide, with its rapidly moving hydroxyl ion, is the least efficient coagulator, whilst sodium iodate with its slow-moving anion is the most efficient coagulator. Using hydrochloric acid and sodium chloride at various temperatures, it is shown that the velocity of coagulation does not depend on the temperature only, because the

Brownian movement of the particles depends on it, but also because the specific coagulation power of the electrolytes changes with the temperature. J. F. S.

Effect of the Wall of Vessels on the Velocity of Gaseous Reactions. Eiichi Yamazaki (*J. Tokyo Chem. Soc.*, 1919, **40**, 606—608).—This is a theoretical paper, attempting to give an explanation for Kooij's work (A., 1893, ii, 569), in which the velocity of dissociation of phosphine was shown to be affected by the nature of the vessel, the ratio of the velocity in the new vessel to that in the old being 1 : 2·25. According to the author, the decomposition of phosphine in a vessel should be considered to be a heterogeneous chemical reaction, that is, (1) a formation of the diffused zone between gas and vessel, (2) chemical reaction. In the new vessel the wall becomes the "diffusion zone," but in the old vessel the decomposition product (phosphorus) adheres to the surface of the vessel, thus creating a larger surface which accelerates the velocity of the diffusion. Ordinarily the velocity of the diffusion of the gas over the wall is so fast that only the velocity of the chemical reaction is measured as the total reaction velocity. The author believes that the vessel acts as a catalyst in the same manner as platinum black or sponge, by removing the product of the reaction, thus maintaining general equilibrium. More detailed investigation and explanation are promised. Chemical Abstracts.

An Unsolved Problem in the Application of the Quantum Theory to Chemical Reactions. W. C. M. Lewis (*Phil. Mag.*, 1920, [vi], **39**, 26—31).—On applying the quantum theory to a unimolecular reaction, it is shown that very different results are obtained according as it is assumed that the absorption of radiation is continuous or discontinuous. A very large discrepancy exists in both cases between the calculated and observed velocity constants, which is much greater on the discontinuous view than on the continuous. This discrepancy is always in the sense that the observed velocity constant is many times greater than the calculated; on the hypothesis of continuous absorption, the observed constant is of the order of 10^7 times greater than the calculated, and also appears to be independent of temperature, for different reactions. The explanation of this discrepancy is expected to throw light on the theory of physicochemical processes. J. R. P.

The Propagation of Flame in Mixtures of Methane and Air. I. Horizontal Propagation. Walter Mason and Richard Vernon Wheeler (T., 1920, **117**, 36—47).

The Propagation of Flame in Complex Gaseous Mixtures. V. The Uniform Movement of Flame in Mixtures of Methane, Oxygen, and Nitrogen. "Maximum-speed Mixtures" of Methane and Hydrogen in Air. William Payman (T., 1920, **117**, 48—58).

Hydrolysis of Iodoacetic Acid. Bror Holmberg (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 11, 1—12).—The velocity of replacement of iodine by hydroxyl in the sodium and barium salts of iodoacetic acid by the action of sodium and barium hydroxides has been studied; the influence of neutral salts (sodium chloride and iodide and barium chloride) was also investigated. The reaction is bimolecular, its velocity being intermediate between those observed for the corresponding bromo- and chloro-acids (compare Johansson, A., 1912, ii, 544). Contrary to expectation, therefore, iodoacetic acid is more stable than bromoacetic acid (compare Drushel and Simpson, A., 1918, i, 57). The effect of the concentration of the metal ions on the velocity constant, C, is given by the equations $C=0{\cdot}106[Na^{\cdot}]^{0\cdot1}$ and $C=0{\cdot}220[ba]^{0\cdot2}$, where $ba=\frac{1}{2}Ba$.

The reaction between iodoacetic acid or its salts and silver nitrate was also studied. The formation of silver iodide takes place much more quickly than the production of acid, and the author concludes that the most important reactions are represented by the equations: $2CH_2I{\cdot}CO_2{}' + Ag^{\cdot} = CH_2I{\cdot}CO_2{\cdot}CH_2{\cdot}CO_2{}' + AgI$ and

$$CH_2I{\cdot}CO_2{\cdot}CH_2{\cdot}CO_2{}' + Ag^{\cdot} = O{<}{\begin{matrix}CO{\cdot}CH_2\\CH_2{\cdot}CO\end{matrix}}{>}O + AgI.$$

If the solutions are not too dilute, the formation of iodoacetylglycollic acid takes place much more quickly than the formation of glycollide. Glycollic acid is then formed indirectly, or it may also be formed directly, according to the equation $CH_2I{\cdot}CO_2{}' + Ag^{\cdot} + H_2O = OH{\cdot}CH_2{\cdot}CO_2{}' + H^{\cdot} + AgI$. T. S. P.

Effect of Chlorine on Periodic Precipitation. [Miss] A. W. Foster (*J. Physical Chem.*, 1919, **23**, 645—655).—When silver nitrate is allowed to diffuse into gelatin films containing potassium chromate, a series of concentric rings is formed, the spacing of which decreases with the distance from the centre. The appearance and spacing of these rings does not depend on the time which has elapsed between the formation of the gelatin film and the addition of the silver nitrate. If, however, a trace of chloride is present in the gelatin the appearance is altered. Making up the gelatin chromate solution with tap water is sufficient to produce the change. If such a film is allowed to harden for three hours and then treated with silver nitrate, the rings are spiral in form and in groups of three. If a little calcium hypochlorite is added to the gelatin and the film allowed to harden for an hour, narrow rings close together are formed by two precipitations. J. F. S.

Some Problems in Contact Catalysis. Wilder D. Bancroft (*Trans. Amer. Electrochem. Soc.*, 1919, **36**, reprint).—A number of specific cases of catalytic reactions are cited where a satisfactory explanation of the mechanism of catalysis is not available, and further study of these is suggested. Thus, the reaction $COCl_2 + H_2O = CO_2 + 2HCl$ is, so far as is known, irreversible. In the presence of excess of water the r[...] n the presence of concentrated hyd[...] ysis is

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negligible. A theory is suggested, but study is necessary to prove it. Also, trichloromethyl chloroformate (superpalite) reacts as follows in the presence of alumina: $CCl_3·O·COCl = CO_2 + CCl_4$, and in the presence of ferric oxide, $CCl_3·O·COCl = 2COCl_2$. The reverse reaction has never been made to take place to any extent. Yet, when some superpalite and ferric oxide were placed in a tube the reaction soon came to an apparent end. When the temperature was raised a little the reaction went further and did not reverse on cooling. It is suggested that this phenomenon was due to poisoning of the ferric oxide. Finally, some experiments by Lind are cited which may, if desired, be regarded as the displacement of an equilibrium by a catalytic agent. If radium emanation is placed in water in the liquid phase, hydrogen and oxygen are formed and escape into the vapour phase; if the emanation is moved up into the vapour phase oxygen and hydrogen are caused to combine. Additional examples are cited and some interesting lines of experiments suggested.

CHEMICAL ABSTRACTS.

Catalytic Decomposition of Hydrogen Peroxide. GÖSTA PHRAGMÉN (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 22, 1—13).—The rate of decomposition of hydrogen peroxide in alkali phosphate or sodium hydroxide solutions has been determined at 17—18°. In the phosphate mixtures, it is shown that the reaction velocity reaches a maximum at $P_H = 11·8$. In alkaline hydroxide solutions, the velocity is not easily reproducible, and sometimes gives a large value and sometimes a small value. Since the velocity decreases with both increasing and decreasing hydrogen-ion concentration, it is assumed that hydrogen peroxide forms a salt with sodium hydroxide which is very stable, and that only the undissociated hydrogen peroxide molecules undergo decomposition. The decomposition of hydrogen peroxide by yeast extract in the presence of a phosphate buffer mixture has been determined at 17—18°. It is shown that fresh yeast decomposes dilute hydrogen peroxide without sending a soluble enzyme into the surrounding liquid. The reaction is of the first order between certain limits, and the reaction coefficient increases proportionally to the quantity of yeast. The catalytic action per cell or per gram can be increased by treating the yeast with sugar solution before use. The reaction constant is no criterion of the quantity of catalase in the cells.

J. F. S.

Catalytic Actions at Solid Surfaces. II. Transference of Hydrogen from Saturated to Unsaturated Organic Compounds in the Liquid State in Presence of Metallic Nickel. E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1919, [*A*], **96**, 322—329. Compare A., 1919, ii, 403).—The evidence that metallic catalysts, during the hydrogenation process, interact primarily with the unsaturated organic compound, together with the resemblance of the whole process to enzyme action (*loc. cit.*), led to the consideration whether the catalytic action, like that

of certain enzymes, might not *be reversible. Evidence in support* of this view has now been obtained. At 180°, an equimolecular mixture of *cyclo*hexanol and methyl cinnamate may, in the presence of nickel, be transformed into one in which about 10% of the cinnamic ester has become hydrogenated to methyl β-phenylpropionate, the *cyclo*hexanol being transformed into *cyclo*hexanone. The experiments indicate that it is necessary that both components of the system should be present in the liquid state. A similar action took place to a certain extent at 230°, when the *cyclo*hexanol was replaced either by dimethyl*cyclo*hexane or by dihydropinene. Similarly, a mixture of ethyl stearate and methyl cinnamate when heated at 230° with catalytic nickel gave a product containing small quantities of methyl β-phenylpropionate and ethyl oleate. An important point to note is that simultaneous dehydrogenation and hydrogenation have now been effected at temperatures not far removed from the general optimum hydrogenation range (170—180°), and that hydrogen has been transferred from one compound to another, instead of from one molecule to another of the same species, as was observed by Zelinski and Glinka (compare A., 1911, i, 870).

There is no absolute proof that the mechanism of the change is not dependent on the production of hydrides of nickel, but the authors prefer to regard it as a further case of the catalytic equilibria, previously discussed, which may be indicated as follows:

$$\begin{matrix}\text{Saturated}\\\text{compound}\end{matrix} + \text{Ni} \rightleftharpoons \left[\begin{matrix}\text{Saturated}\\\text{compound, } Ni\end{matrix}\right] \rightleftharpoons$$

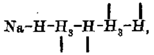
$$\left[\begin{matrix}\text{Unsaturated compound, Ni}\\\text{hydrogen}\end{matrix}\right] \rightleftharpoons \begin{matrix}\text{Unsaturated}\\\text{compound}\end{matrix} + \text{Ni} + H_2.$$

The ultimate equilibrium will depend on the resultant of the varying affinity for nickel of the saturated and unsaturated compounds involved.

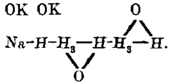
This view of catalytic hydrogenation and dehydrogenation affords some explanation of the products obtained (compare Moore, *J. Soc. Chem. Ind.*, 1919, **38**, 320T) during the hydrogenation of unsaturated glycerides, where partial isomerisation occurs. It is suggested that, in the hydrogenation of ethyl oleate, a portion of the freshly produced ethyl stearate in contact with the nickel undergoes dehydrogenation, the hydrogen liberated being transferred to more ethyl oleate, the "dehydrogenated ethyl stearate" formed being the ethyl Δ^{λ}-oleate isolated by Moore (*loc. cit.*). W. G.

Constitution and Structure of the Chemical Element. HAWKSWORTH COLLINS (*Chem. News*, 1919, **119**, 295—296).—Single electropositive charges emanate from masses of 1 (hydrogen), 7 (lithium), 23 (sodium), and 39 (potassium), also two electropositive charges emanate from 4 (helium), of which one has been shown to emanate from a mass 3 (H_3), hence single electropositive charges emanate from masses 1, 3, 7, 23, 39. Taking the first twenty-six elements, it is shown that twenty of these may have their

atomic weights split up into the above-named numbers in such a way that the number of parts is the same as the maximum valency. All the parts are odd numbers, and the non-metallic elements are characterised from the metallic by the presence of one or more portions (1 + 3) (helium). Electropositive forces are distinguished from electronegative forces by the following rule: an electropositive force emanates from each of the masses 1, 3, 7, 23, 39, except when an element has one or more portions (1 + 3), in which cases electropositive forces emanate from these portions, whilst electronegative forces emanate from each of the remaining portions of the element. Hydrogen forms the connecting link in the structure of these elements. From tables given in the paper, it is shown that the longer the chain of $-H-H_3$, the more volatile the element and the stronger the electronegative forces from the metallic portions. On this basis, the structure of the sulphur atom is given as



in which Na represents 23, H represents 1, and H_3 3. The thick lines represent electropositive charges, the curly lines electronegative charges, and the thin lines forces which are not chemically evident, but which have to be overcome before the element can be disintegrated. The atomic number of sodium is 11, that of H and H_3 unity, which makes the atomic number of sulphur 16, which is in keeping with fact. The formula therefore shows the connexion between atomic weight, atomic number, and maximum valency, and distinguishes between electropositive and electronegative charges. The molecule K_2SO_4 may therefore be represented:



J. F. S.

A Model of Radioactive Atoms. Torahiko Terada (*Proc. Phys. Math. Soc. Japan*, 1919, [3], **1**, 185—195).—According to the recent view of atomic structure, an atom consists of a positive nucleus about which a number of electrons are revolving. The conception of the positive nucleus is slightly extended by considering the case of two heavy nuclei with opposite charges revolving about the common centre of mass. Assuming a primary with the larger mass having a positive resultant charge, and the secondary of smaller mass charged negatively as a whole, and leaving out of consideration the ring electrons, it is evident that the two members of the nuclear system will exert on each other a mutual action analogous to the tidal action in the case of the gravitating planetary system. Both members are considered to consist of a number of positive and negative elementary charges, bound together by some unknown forces; also most of the positive charges are assumed to

consist of two elementary charges, as in the case of α-particles. When the tidal action exceeds a certain limit, the secondary may become unstable, and when the elementary charges in the two substances happen to take a definite configuration, one of the charges may escape and be projected from the nuclear system with the momentum possessed during the orbitual motion. If the negative secondary loses a positive charge by the expulsion of an α-particle, the attraction of the primary will increase, and the orbitual velocity be accelerated. In actual radioactive transformations, the velocities of the expulsion of the α-particles generally increase with successive transformations, although with some exceptions. The tidal action will increase with the decreasing distance between the two nuclei, and consequently the chance of disruption will increase, because the chance of the α-particle steppiug out of the critical threshold will increase. The result will be the shortening of the life of the atom in question. This seems to suggest a possible way of explaining Geiger and Nuttall's law concerning the relation between tbe average lives of radio-elements belonging to a disintegration series and the velocities of the α-particles emitted from these elements. If the two members of the nuclear system gradually approach each other by successive emission, a stage may be attained at which the two substances are amalgamated into one, provided the resulting configuration is a stable one. When this final stage is reached, the disintegration will be stopped and the end-product of the radioactive transformation will be reached. One of the simplest systems conceivable is proposed as a provisional working model, and the consequences tested in the light of the available experimental data. CHEMICAL ABSTRACTS.

Metals and Non-metals. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 119—125).—The author explains the positive charge of the chlorine electrode by assuming that the chloriue atom has the power of splitting off and absorbing electrons, and, further, that these two processes can take place side by side. This is represented by the equations $XCl_{2G} \rightleftharpoons 2XCl_{G}' + 2X\ominus_{G}$ and $YCl_{2G} + 2Y\ominus_{G} \rightleftharpoons 2YCl_{G}'$, in which X and Y indicate the fractions of the chlorine molecules which have undergone positive and negative ionisation respectively. As the electrons which are absorbed in the second action proceed from the first, it is clear that $Y \leqq X$, but, chlorine being a non-metal, both fractions must be extremely small. If, then, it is further assumed that the negative ions almost exclusively pass into solution, the electrode will then possess a positive charge. Extending the above hypothesis, the author shows that there is only a difference of degree between metals and non-metals, and not one of kind. If it be assumed that all elements can both split off and absorb electrons, then the factor X is comparatively large for metals and small for non-metals, and for non-metals Y is exceedingly small. This view is in keeping with the large electric conductivity of metals and the small conductivity of non-metals. In the case of the metals, the

positive ions have the greater solubility, and the negative ions in the case of the non-metals. This is in keeping with the different electromotive behaviour of metals and non-metals. The difference in solubility between the two ions is so great as to justify the assumption that only one kind is present in solution. Amphoteric elements probably send appreciable quantities of both positive and negative ions into solution. J. F. S.

Atomic Structure and the Periodic Law. TYCHO E:SON AURÉN (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 18, 1—7).—A theoretical paper. The author's experiments on the absorption of Röntgen rays (details not yet published) indicate the possibility of differentiating between the inner and outer electrons in the atom, the outer electrons being identical with the so-called valency electrons and playing a totally different rôle from the inner electrons. In accordance with this view, Kossel's table (A., 1916, ii, 243) for the first twenty-three elements of the periodic system is modified. The number of electrons in the outer ring increases from one in the case of hydrogen to seven in the case of nitrogen; it does not become eight in the case of oxygen, but four electrons go from the outer ring to the inner system; the number of outer electrons then increases to seven again for sodium, whilst for magnesium four more electrons go from the outer to the inner system, and so on. The consequences of these conceptions are discussed, special reference being made to the valencies of the elements in the various groups. For example, it is argued that sulphur should be bivalent; the existence of SO_3 and SF_6 is no definite proof of the sexavalency of sulphur, since the former can be represented by a ring structure and the latter as $\genfrac{}{}{0pt}{}{F}{F}{>}F{\cdot}S{\cdot}F{<}\genfrac{}{}{0pt}{}{F}{F}$. T. S. P.

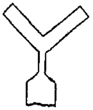
Atomic Numbers. HAWKSWORTH COLLINS (*Chem. News*, 1919, **119**, 285—287).—The author considers the atomic weights (nearest whole number), atomic numbers, and valencies of the first twenty-eight elements, taken in order of their atomic weights. It is shown that, with four exceptions (glucinum, nitrogen, scandium, and cobalt), when the atomic weight is represented by an even number, the maximum valency and the atomic number are both represented by even numbers, and when the atomic weight is represented by an odd number, the valency and the atomic number are also represented by odd numbers. Further, the elements, with the exceptions named, follow one another alternately odd and even. The probability that this condition of things has happened accidentally is $1:4^{28}$. The reason for the odd and even rule is shown to be as follows. If the atomic weight of an element be split up into 3's and 1's alternately, always commencing with a 3, the number of portions obtained gives the atomic number, and should the atomic number be an even number, the atomic weight must of necessity be an even number, but if the atomic number is odd, the atomic weight must also be odd. The atomic number is exactly

obtained as follows. If the atomic weight is an even number, the atomic number is one-half of the atomic weight, but if the atomic weight is an odd number, the atomic number is one-half of the atomic weight from which 1 has been subtracted. J. F. S.

The Mathematical Possibility of Increasing the Yield or of Reducing the Proportion of the Reacting Substances in certain Chemical Reactions. ANGEL PÉREZ HERNÁNDEZ (*Anal. Fis. Quim.*, 1918, **16**, 302—317).—An elementary mathematical method is illustrated for the construction of chemical equations in which two or more reactions are simultaneously involved. W. S. M.

Some Biographical Notes on Hermannus Follinus. W. P. JORISSEN (*Chem. Weekblad*, 1919, **16**, 947—951).—The biographer gives a very brief sketch of Hermannus Follinus, who was born in Friesland, *circa* 1590, and joined the medical faculty in Cologne, where he died of the plague in 1622. He was the author of "Den Nederlandtsche Sleutel van't Secreet der Philosophie" (Key to the Secrets of Philosophy), "Physiognomie," and "Simonides, ofte die Memori-const" (Science of Memory). W. J. W.

An Apparatus for Preparing in a Very Short Time Homogeneous Liquid Mixtures. PIERRE JOLIBOIS (*Compt. rend.*, 1919, **169**, 1095—1098).—A simple apparatus is described consisting essentially of two containers, one for each of the liquids to be mixed, arranged so as to deliver into the two limbs of a Y-tube of the pattern shown the liquids in the requisite proportion. The diameter of the Y-tube is 6·2 mm., and the lower limb has a restriction as shown 1·5 mm. in diameter and 2 cm. long. With such an apparatus a homogeneous mixture may be obtained from two miscible liquids in 1/100th of a second. W. G.



Eykman's Suction Pump. L. TH. REICHER (*Chem. Weekblad.*, 1919, **16**, 951—956).—This apparatus embodies the principle of Geissler's suction pump, but the operation of filling the vessel in communication with the apparatus which has to be exhausted, by lifting a second vessel periodically, is avoided. Special features of Eykman's pump are a "vacuum reservoir," containing air-free, concentrated sulphuric acid, and a drying device also filled with that liquid. A sketch of the complete apparatus is given and its mode of operation described. W. J. W.

Inorganic Chemistry.

Model of a Triatomic Hydrogen Molecule. N. BOHR (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 28, 1—16).—A theoretical paper in which it is shown that triatomic hydrogen consists of three nuclei and three electrons. The electrons rotate at equal angular intervals in a common circular orbit, whilst the three nuclei are placed on the axis of this orbit. It is shown that H_3 cannot be formed from H_2 molecules without the supply of energy from external sources. On the other hand, it is shown that in hydrogen gas which is ionised by external agencies, molecules of H_3 may be formed by successive processes, each of which is accompanied by the production of heat. J. F. S.

The Solubility of Sulphur Dioxide in Sulphuric Acid. FRANK DOUGLAS MILES and JOSEPH FENTON (T., 1920, **117**, 59—61).

Some Points of View concerning the Nitrogen Question and Related Problems. L. HAMBURGER (*Chem. Weekblad*, 1919, **16**, 560—595).—An amplified version of a lecture delivered before the Algemeen Bestuur der Nederlandsche Chemische Vereeniging on July 13th, 1918. W. S. M.

Electrochemical Reactions of Nitrogen and the accompanying Spectroscopic Phenomena. L. HAMBURGER (*Chem. Weekblad*, 1918, **15**, 931—942).—A mixture of nitrogen and hydrogen in stoicheiometrical proportions under a pressure of 12 mm. of mercury was passed through a quartz capillary tube and subjected to a direct-current discharge of 12 amperes per square cm. A yield of 109 mg. of ammonia per kilowatt-hour was obtained. Reduction of the current density and simultaneous increase of the time of exposure to the discharge gave much smaller yields. The conditions for a high yield of ammonia thus correspond with those necessary for the formation of activated atomic nitrogen and hydrogen. The discharge through mixtures of nitrogen with hydrogen, oxygen, and carbon monoxide was examined spectroscopically. In every case evidence of the disruption of the molecules and formation of new compounds, such as cyanogen, was obtained. W. S. M.

The Dissociation Constant of Nitrogen Peroxide. EUGÈNE WOURTZEL (*Compt. rend.*, 1919, **169**, 1397—1400).—As a result of measurements at temperatures between 0° and 86·5° it is shown that the variation of the dissociation constant with the temperature is given by $\log K/T = 8{\cdot}9908 - 2810{\cdot}5/T$, and calculated from this the heat of polymerisation is 12,850 cal., exact to 0·5%. W. G.

Luminescence and Ionisation in the Oxidation of Phosphorous Oxide. HERMAN RINDE (*Arkiv Kem. Min. Geol.*, 1917–18, **7**, No. 7, 1—21).—A mixture of oxygen and carbon

dioxide, dried by means of sulphuric acid, calcium chloride, and phosphoric oxide, and warmed to a suitable temperature, is passed through two absorption bulbs containing phosphorous oxide, with the vapour of which it becomes saturated. No luminescence takes place with the dried gas, but when the mixture is led over the surface of water contained in a test-tube, luminescence appears. The absorption bulbs and test-tube containing water were immersed in a thermostat at constant temperature, and the total intensity of the luminescence was measured photographically by means of a Martens' photometer.

There is no luminescence in pure carbon dioxide, but the addition of oxygen causes the phenomenon to appear, and its intensity is greatest in mixtures containing 5% of oxygen. With increase in the percentage of oxygen the intensity decreases and attains an approximately constant value between 50% and 100% oxygen (compare Scharff, A., *1908, ii, 373*). When a tube, 3·75 metres long, is inserted between the absorption bulbs and the test-tube, the intensity of the luminescence is about the same for mixtures containing a low percentage (about 5%) of oxygen, but it rapidly diminishes with increasing oxygen content to a lower value than before the tube was inserted. At the same time the tube becomes covered with a deposit of phosphoric oxide. These results indicate that the phosphorous oxide is oxidised without luminescence by the dry oxygen, and that the diminished luminescence with mixtures containing high percentages of oxygen is due to the fact that the gas coming into contact with the water-vapour contains much less phosphorous oxide.

According to Scharff (*loc. cit.*), the merest trace of water-vapour is sufficient to cause luminescence, but the author finds that when the vapour pressure of the water-vapour is diminished, as, for example, by using concentrated sulphuric acid instead of water, the luminescence becomes very feeble.

As with all gas reactions, the width of the test-tube containing the water affects the intensity of the luminescence. The wider the test-tube the less the luminescence.

The author suggests that in dry oxygen phosphorous oxide is directly oxidised to phosphoric oxide, but that in moist oxygen an intermediate compound, X, is formed, according to the equation $P_4O_6 + H_2O + O_2 \longrightarrow X \longrightarrow H_3PO_4$.

Ionisation does not occur in a gas free from oxygen, but containing phosphorous oxide. In the presence of oxygen ionisation takes place, and the author has measured the saturation current (compare Harms, A., 1904, ii, 331; Bloch, A., 1905, ii, 72). The ionisation is not a photoelectric effect, as shown by measurement of the saturation current with different electrodes, but is caused by the oxidation of an unknown intermediate product formed from phosphorous oxide and water vapour. The mobility of the ions is small compared with that of ordinary gaseous ions, but of the same order as that obtained for the ions formed in the oxidation of phosphorus (compare Harms and Bloch, *loc. cit.*), and it is very probable that the ions are produced by the same reaction in both cases. T. S. P.

Some Chemical Characters of Ancient Charcoals. T. C CANTRILL (*Archaeol. Cambrensis*, 1919, 365—392).—Although the pieces of charcoal or charred wood found during archæological excavations are more readily attacked or dissolved by such reagents as nitric acid and potassium chlorate, and hypochlorite solution, thus differing from modern, well-burnt charcoal, the author considers that the solubility, etc., of some of the ancient charcoals is simply due to their incomplete carbonisation, and that there is doubt that they were produced by the agency of fire. The situations in which certain of the charcoals are found negatives the opinion that the blackening of wood was due to the action of peaty soil. W. P. S.

Artificial Production of Diamond. SIR CHARLES ALGERNON PARSONS (*Phil. Trans.*, 1919, *A*, **220**, 67—107).—Bakerian lecture. It is shown from experiments that all the hydrocarbons, chlorides of carbon, and oxides of carbon deposit amorphous carbon or graphite on a carbon rod electrically heated at any pressure up to 4400 atms. and in a few cases up to 6000 atms. At 15,000 atms. carbon and graphite electrically heated are either transformed into soft graphite or are first vaporised and condensed as such. The experiment of compressing a mixture of acetylene and oxygen and the production of a temperature in excess of that required to vaporise carbon, accompanied by a momentary pressure of 15,000 atms., shows that the failure to convert graphite into diamond is not due to lack of temperature. The experiment of firing a high-velocity steel bullet with cupped nose through vaporising carbon into a hole in a block of steel raises the pressure momentarily to 300,000 atms. and the temperature probably 1000°, but the fact that only a few minute crystals resembling diamond were produced (probably from the iron) leaves a doubt as to whether the duration of the pressure was sufficient to start a recognisable transformation of graphite to diamond. A repetition of many of the experiments, in which diamond has been claimed to be formed, has given negative results except where iron has played a part. A list of the experiments tried together with conditions and results is given in an appendix to the paper. In repeating Moissan's experiments it is shown that when a crucible of molten iron is subjected to pressure more than three times as great as can be produced by these contractile forces, the yield of diamond is not increased; on the other hand, if the occluded gases are imprisoned, then the yield of diamond is about the same as when the crucible is plunged into water, whilst if the conditions are such as to allow a free passage of the gases through the skin of the ingot the yield is at once reduced, even though the bulk pressure on the ingot is the same. Experiments in vacuum, from 75 mm. to *X*-ray vacuum, show generally that as the pressure is decreased the yield of diamond is diminished, and below 2 mm. no diamond could be detected. The greatest percentage of diamond occurred when the atmosphere round the crucible consisted of 95% carbon monoxide, 1% hydrogen, 2% hydrocarbons, 2% nitrogen. The weight of diamond is about 1/20,000 of the weight of the iron. It appears that the formation of diamond in rapidly cooling iron takes

place when it is solid or in a plastic condition or even at a lower temperature. The rapid pitting of a diamond in highly carburised iron just above its melting point is so pronounced that the largest diamond hitherto produced artificially would be destroyed in a few seconds if the iron matrix were molten. The experiments indicate that the bulk pressure on the metal does not play a part in the formation of diamonds, but that the previous heat treatment, the impurities in the iron, and the condition of the gases within the metal are the important factors. The iron in the most successful experiment has a concentration of diamond 270 times as great as the blue ground in the South African mines. J. F. S.

Production of Carbon Monoxide in the Flames of Gases. André Kling and Daniel Florentin (*Compt. rend.*, 1919, **169**, 1404—1406).—A number of gases, the carbon monoxide content of which varied from 0% to 60%, were burnt at differing types of burners in a large chamber, and the carbon monoxide in the air was estimated at the end of one hour. The results indicate that the production of carbon monoxide is due principally to the sudden cooling of the flame. For a given type of burner the amount of carbon monoxide present in the gas to be burnt is without influence on the amount present in the products of combustion. The Auer burner produced comparatively large amounts of carbon monoxide, this production being due apparently to the presence of the incandescent mantle. The hourly production of carbon monoxide with certain common types of burners is sufficiently high to warrant further efforts to improve them. W. G.

Atomic Structure of Metals in Solid Solution. A. L. Feild (*Chem. and Met. Eng.*, 1919, **21**, 566—570).—The reason for the difference in physical properties of solid solution alloys and their components has been investigated. It is concluded that the alloys retain in the solid state the same atomic structure as in the liquid state, the metals being in the amorphous form. Such a solid solution is analogous to a supercooled liquid with the same electrical resistance and temperature-coefficient of resistance as in the molten state. Experiments with alloys of nickel and chromium, and of gold and silver, confirm this theory. It does not apply to eutectic alloys. The hardness of alloys is also ascribed to an amorphous state.
W. J. W.

Transition of Dry Ammonium Chloride. Alexander Smith, Herbert Eastlack, and George Scatchard (*J. Amer. Chem. Soc.*, 1919, **41**, 1961—1969).—Time-temperature curves, both heating and cooling, have been made for absolutely dry ammonium chloride with the object of ascertaining whether the dry material changes into a second crystalline form at 184·5°, as does the undried material. It is shown that ammonium chloride which has been dried for forty-five days at 155—165°, or for three years with phosphoric oxide in a high vacuum, undergoes exactly the same transition at 184·5° as the undried salt. In the thermal measure-

ment of transition points in a high vacuum confusion may result from the greater thermal effects of distillation. Wegscheider's explanations of the anomalous vapour density of dried ammonium chloride by a failure to undergo transition in the absence of water are untenable in the light of these results (A., 1918, ii, 298).

J. F. S.

Lithium Silicate. K. ALB. VESTERBERG (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 30, 1—9).—Amorphous silicic acid, which has been dried at 100°, dissolves slowly in a fairly concentrated (approx. 2*N*) solution of lithium hydroxide at the ordinary temperature, giving finally a solution containing 3·4 mols. of SiO_2 to 1 mol. of Li_2O. Thus lithium behaves similarly to potassium and sodium in giving soluble silicates containing a large excess of acid over the base (compare A., 1915, ii, 344; also Jordis and Kanter, A., 1903, ii, 475, 542, 595; Jordis, 1908, ii, 291; Ordway, 1908, ii, 37). In warm lithium hydroxide solution, however, silicic acid is almost insoluble, the acid being transformed into a practically insoluble lithium silicate.

Lithium metasilicate occurs in two modifications, the one easily soluble and the other almost insoluble. The latter, which has the formula Li_2SiO_3,H_2O, is obtained as a white, granular precipitate when a fairly concentrated solution of sodium metasilicate is mixed with the equivalent quantity of lithium chloride, lithium hydroxide added in approximately normal concentration, and the solution heated for a short time at 80—90°. It can also be obtained by dissolving silicic acid, which has been dried at a temperature not higher than 100°, in twice the theoretical amount of 2*N*-lithium hydroxide solution at the ordinary temperature, and then heating the solution for a short time at 80°.

T. S. P.

A New Physicochemical Method of Analysis of Precipitates. Application to the Study of the Calcium Phosphates. PIERRE JOLIBOIS (*Compt. rend.*, 1919, **169**, 1161—1163).—The two solutions, from which the precipitate is obtained, are very rapidly mixed by means of the apparatus previously described (this vol., ii, 107), and the precipitate is collected and analysed and the supernatant liquid is also analysed when equilibrium has been reached. Applying this method to the study of mixtures of solutions of *calcium hydroxide and phosphoric acid in varying proportions*, the author has prepared and characterised a new calcium phosphate having the composition $2CaO,P_2O_5,3CaO,P_2O_5,10H_2O$. This phosphate occurs in a crystalline form, and in the presence of excess of phosphoric acid is slowly converted into the dicalcium phosphate.

W. G.

Research on Magnesia Alba by Joseph Black, Petrus Driessen and Others. W. P. JORISSEN (*Chem. Weekblad*, 1919, **16**, 1579—1589).—The author gives a retrospect of the researches of Joseph Black on magnesia alba, which led to his discovery of carbon dioxide ("fixed air"). The methods of preparation of

magnesia alba, described in the literature on the subject, are variations of the original experiments of Black, Driessen, and other investigators of the eighteenth century. W. J. W.

Zincates of Sodium. Equilibria in the System Na_2O-ZnO-H_2O. F. GOUDRIAAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 179—189).—The solubility isotherm in the system Na_2O–ZnO–H_2O has been completely determined at 30° by dissolving zinc oxide in solutions of sodium hydroxide of various concentrations and determining the solubility. The following substances appear as stable, solid phases: zinc oxide, sodium zincate, $Na_2O,ZnO,4H_2O$, and the monohydrate of sodium hydroxide. Sodium zincate forms very strongly incongruent solutions; in solutions containing 1 part of sodium hydroxide to 2 parts of water, it is decomposed, with separation of zinc oxide. Amorphous, gelatinous zinc hydroxide is to be regarded as a phase of a varying water content; it is impossible to remove all adsorbed ions from it, and it is metastable as regards zinc hydroxide. In special circumstances zinc hydroxide may be obtained as a crystalline phase of the constant composition, $Zn(OH)_2$. This crystallised hydroxide is metastable at 30° with respect of zinc oxide. J. F. S.

Reguline Lead Peroxide. WILH. PALMAER (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 31, 1—15).—Compact lead dioxide has been prepared by the electrolysis of lead nitrate solution. The product is greyish-black in colour and has a pronounced crystalline appearance, and contains no impurities; it has a hardness 5—6 and D 9·360. In all respects it is similar to the mineral plattnerite. The specific resistance at 18° is 0·000845 ohm and the specific conductivity 1180 ohm^{-1}. The temperature-coefficient of the conductivity is 1/8% per degree. J. F. S.

Aluminium Spontaneously Oxidisable in the Air. E. KOHN-ABREST (*Compt. rend.*, 1919, **169**, 1393—1395).—Attention is drawn to the fact that when aluminium is distilled in a vacuum at 1100°, the globules of aluminium remaining undistilled at the end of sixteen to twenty hours, when exposed to the air at the ordinary temperature, undergo spontaneous oxidation, giving a yellowish-grey powder, which is a mixture of the oxide and the finely divided metal. This aluminium only contained 0·4% of iron and 0·5% of silicon. W. G.

Chemical Method for the Determination of the Strength of Sparingly Soluble Inorganic Bases. K. A. VESTERBERG (*Arkiv. Kem. Min. Geol.*, 1917, **6**, No. 11, 1—20).—The determination of the hydrolysis of salts of sparingly soluble inorganic bases by electrometric methods and methods depending on the inversion of sucrose or the hydrolysis of esters has given very varying results, according to the methods used (compare Denham, T., 1908, **93**, 41; Lundén, A., 1908, ii, 164). Farmer's method (T.,

1901, **79**, 863) for the determination of hydrolysis does not give correct values, owing to the disturbance of the hydrolytic equilibrium by the partial extraction of the one product of hydrolysis. In the case of cobalt acetate, for example, too little acetic acid is extracted. The author makes use of Farmer's method, but modifies and corrects it as follows. The solution is extracted with twice its volume of ether; the same ethereal solution is again used to extract half its volume of a fresh solution of cobalt acetate. This process is repeated until the concentration of the ether phase becomes constant with respect to acetic acid, showing that it is in equilibrium with hydrolysed cobalt acetate solution, in which base and acid are present in equivalent proportions. The percentage hydrolysis can then be readily calculated. Usually, the concentration of the ether phase becomes constant after three extractions.

Corrections have to be made for the increase in volume of the aqueous phase by solution of ether, and the ether and salts used have to be specially purified. If the acetate is difficult to obtain pure, accurate results can be obtained by using a solution of the sulphate or nitrate to which an equivalent quantity of sodium acetate has been added.

The determinations were carried out at 18°, the distribution coefficient of acetic acid between ether and water being taken as 2·1. The results obtained for percentage hydrolysis were as follows: *N*/2-cobalt acetate, 0·19; *N*/5, 0·165; *N*/2-nickel acetate, 0·435; *N*/5, 0·38. It follows that cobalt hydroxide is a stronger base than nickel hydroxide, and this agrees with the stabilities of their sulphates. The fact that the hydrolysis is greater in the stronger solutions may be due to the greater salting-out effect of the acetate on the acetic acid.

The hydrolysis of lanthanum acetate in *N*/5-solution was 0·315% and in *N*/10-solution 0·286%, the value 0·31% being taken as correct for both solutions, the differences being within the error of experiment. Lanthanum acetate was found to have $1\frac{1}{2}H_2O$ of crystallisation, the solubility at 18° being 20·43 grams of the anhydrous salt in 100 grams of water; it loses $\frac{1}{2}H_2O$ at 100°. T. S. P.

A New Complex Form of Chromic Sulphate. A. Recoura (*Compt. rend.*, 1919, **169**, 1163—1166).—When a *N*/2-solution of chromic sulphate is allowed to remain until equilibrium is reached, in so far as the formation of the green sulphate is concerned, and then evaporated to saturation point in a vacuum, on the addition of an excess of alcohol a lilac-grey precipitate is formed. If this precipitate is immediately collected and washed with a little ether, it is found to contain $18H_2O$ and to have the whole of its $''SO_4$ precipitable by barium chloride. It changes, however, spontaneously and rapidly when exposed to the air, and at the end of the day contains only $16H_2O$, and gives no precipitate with barium chloride. If left in a desiccator, its water content finally drops to $12H_2O$. The constitution of this new complex sulphate has not yet been determined. W. G.

Method of Obtaining, and Optical Study of, Crystals of Sodium Chromate Tetrahydrate. LUCIEN DELHAYE (*Bull. Soc. franç. min.*, 1918, **41**, 80—92).—Deliquescent monoclinic crystals 5 mm. in length can be obtained by allowing a solution of sodium chromate saturated at 50° to cool to about 27°, filtering, and keeping for several days with occasional shaking. The refractive indices, optic axial angle, dispersion, etc., have been measured for light of various wave-lengths. CHEMICAL ABSTRACTS.

Chemistry of Quinquevalent Tungsten. OSCAR OLSSON COLLENBERG (*Arkiv. Kem. Min. Geol.*, 1918, **7**, No. 5, 1—35).—Solutions of tungstic acid and alkali tungstates in oxalic acid or alkali oxalate solutions are readily reduced to quinquevalent tungsten derivatives. From the solution of tungstic acid in oxalic acid, pure, solid reduction products could not be isolated, but if the solutiou is saturated with hydrogen chloride and then treated with a solution of rubidium chloride in concentrated hydrochloric acid, the compound *dirubidium pentachlorotungstite*, Rb_2WOCl_5, crystallises out in very good yield. When a solution of an alkali tungstate in oxalic acid solution containing a slight excess of alkali oxalate is reduced with tinfoil, the colour passes through dark blue and becomes green, yellowish-green, and finally red. On cooling the highly concentrated solution, oxalic acid, alkali oxalate, and tin oxalate separate. The tin is removed by hydrogen sulphide from the solutiou, and, on adding alcohol, a dark reddish-brown powder separates. On dissolving the powder in water and adding an excess of alkali iodide or bromide, it is obtained pure. In this way, the *oxalo-tungstites* of *sodium*, *potassium*, and *ammonium* have heen prepared. The potassium salt has the formula

$$3K_2O,2W_2O_3,4C_2O_3,9H_2O,$$

whilst the sodium salt is similar, except that it contains $12H_2O$. The oxalo-tungstites are suitable substances for the preparation of other quinquevalent tungsten derivatives. They dissolve readily in hydrochloric acid to produce deep blue solutions, from which the oxy-chlorides of quinquevalent tungsten may be separated. They are soluble in potassium thiocyanate solution, producing deep red-coloured solutions; they dissolve in concentrated hydrofluoric acid solution, producing violet solutions. On boiling with potassium cyanide, yellow solutions are obtained, from which double cyanides of the type $M_4W(CN)_8$ may be isolated. The alkali oxalo-tungstites may be converted into chloro-tungstites by the following methods: (*a*) by treating the hydrochloric acid solution of an alkali (K or NH_4) oxalo-tungstite with hydrogen chloride, (*b*) by adding chlorides (rubidium, cæsium, aniline, tetraethylammonium, and tetrapropylammonium) to the hydrochloric acid solution of an oxalo-tungstite, and (*c*) by adding either pyridinium chloride or quinolinium chloride to a solution of ammonium chloro-tungstite in concentrated hydrochloric acid. By these methods, derivatives of the types: (i) $M_2WOCl_5(M = NH_4, Rb, Cs, C_6H_5{\cdot}NH_3)$,

(ii) $M_2WOCl_5,xH_2O(M = K)$,

(iii) $MWOCl_4$($M = C_5H_5NH$, C_9H_7NH), and (iv) $MWOCl_4,H_2O$($M = [C_2H_5]_4N$, $[C_3H_7]_4N$), have been prepared. All the derivatives obtained have been shown by titration with potassium permanganate or by titration with iodine and arsenious acid to contain the *tungsten in the quinquevalent condition*. The *chloro-tungstites* are finely crystalline powders; they are quite stable in dry air, but at 60—70° are oxidised, turning blue, and eventually quite white. They are hydrolysed by water, and a reddish-brown hydroxide is produced. In the case of the less soluble compounds, for example, the cæsium salt, Cs_2WOCl_5, the hydrolysis is not complete. The chloro-tungstites are soluble in concentrated hydrochloric acid, and in the case of the metal derivatives the solubility decreases with increasing atomic weight; they are insoluble in most organic solvents, except in the case of the rubidium and cæsium derivatives, which are soluble in absolute methyl and ethyl alcohol. The solubility in methyl alcohol is very much greater than in ethyl alcohol. Oxidising agents convert the chloro-tungstites into sexavalent tungsten derivatives. A vigorous reaction takes place on treatment with potassium cyanide, with the production of double cyanides of the type $M_4W(CN)_8$. The compounds of the type (iii) and (iv) are regarded as derivatives of metatungstous acid, $O_2W{\cdot}OH \longrightarrow Cl_4W{\cdot}OH$, whilst those of types (i) and (ii) are regarded as derivatives of orthotungstous acid, $W(OH_5) \longrightarrow (HO)_2W(OH)_3 \longrightarrow {}^{HCl_2}_{HO}{>}WCl_3$. For the special description and preparation of the individual chloro-tungstites, the original should be consulted.

J. F. S.

Decomposition of Stannous Chloride by Water and by Potassium Hydroxide Solutions. C. M. CARSON (*J. Amer. Chem. Soc.*, 1919, **41**, 1969—1977).—Making use of the principles of the phase rule, the author has investigated the action of water and potassium hydroxide on stannous chloride. The experimental results show that the compound, $2SnCl_2,7Sn(OH)_2$, is the most basic of all the basic stannous chlorides. A slightly variable, crystalline material of approximately the formula $3SnCl_2,5SnO,3H_2O$ is the *precipitate commonly formed by the action of boiling potassium* hydroxide on an excess of stannous chloride, and there is no compound of intermediate composition. Whether any basic compound lies between $3SnCl_2,5SnO,3H_2O$ and the normal salt was not determined. The precipitates usually formed by the action of water on stannous chloride contain such a large proportion of stannic compound that the analyses are of no value in ascertaining the composition of the basic stannous chlorides. J. F. S.

The Peroxides of Bismuth. RICHARD ROBERT LE GEYT WORSLEY and PHILIP WILFRED ROBERTSON (T., 1920, **117**, 63—67).

Behaviour of Hydrogen towards Rhodium. A. GUTBIER and O. MAISCH (*Ber.*, 1919, **52**, [*B*], 2275—2280).—The experi-

ments were performed in the same manner as with palladium, iridium, and platinum (A., 1913, ii, 608; 1919, ii, 367, 368). The results may be summarised in the following manner. The deep black modification, rhodium-black, is able to absorb far more hydrogen than any other form. The maxima of hydrogen absorption amounted to 180 volumes at 190° for the greyish-black form, 165 volumes at 40° for the slightly greyish-black variety, and 206 volumes at 0° for the deep black modification. (The varieties are obtained in the order given by the reduction of sodium rhodium chloride by hydrazine in faintly acid, neutral and ammoniacal solution respectively; the purest preparations, dried in a vacuum over phosphoric oxide, contained about 3% of water and 0·3% of oxygen.) The absorption of hydrogen by rhodium is much less than by palladium, and corresponds with that observed with platinum. Spongy rhodium, like spongy platinum, only absorbs small amounts of hydrogen. H. W.

Mineralogical Chemistry.

Hausmannite in the Batesville District, Arkansas. H. D. MISER and J. G. FAIRCHILD (*J. Washington Acad. Sci.*, 1920, **10**, 1—8).—The abundant manganese ores of this district consist of the oxides *psilomelane*, *hausmannite*, braunite, manganite, pyrolusite, and wad, the first two, which occur intimately intergrown, being the commonest. They occur as irregular masses, weighing from less than a pound to 22 tons, embedded in clay, limestone, shale, sandstone, etc. The hausmannite, however, occurs as a replacement material only in the limestone, and as a residual material in clay derived from limestone. Analysis I is of a sample from the W. T. Gray mine near Pfeiffer, and II from Club House mine, near Cushman; they correspond with hausmannite (Mn_3O_4) with 13% and 31% admixed psilomelane respectively.

	MnO.	O.	Fe_2O_3.	Al_2O_3.	SiO_2.	CaO.
I.	91·38	7·78	Nil.	Nil.	Nil.	Trace
I.	90·40	8·87	0·48*		0·10	Trace

	MgO.	BaO.	H_2O.	Total.	Sp. gr.
I.	Trace	0·26	0·62	100·04	4·836
I.	Trace	Nil.	1·03	100·88	4·778

* Fe_2O_3 *trace.*

The 'braunite' described by Penrose in 1891 is shown to be such mixture of hausmannite and psilomelane. Braunite is readily istinguished by the fact that it yields considerable gelatinous ilica. L. J. S.

Analyses of Dolomites. ALBERT ROTHROCK and J. B. SHUMAKER (*Chem. News*, 1920, **120**, 29—31).—The following analyses of dolomite rocks and dolomitic limestones from various localities show considerable variations from typical dolomite, $CaMg(CO_3)_2$, which contains $CaCO_3$ 54·35%, $MgCO_3$ 45·65%. I, white, compact, crystalline, from Ossining, New York. II, dark grey, massive, from Cumberland. III, light-coloured, massive, from Cerro Gordo, Inyo Co., California. IV, grey, compact with conchoidal fracture, from Frankenstein, Silesia; this approaches magnesite. V, white, compact, and crystalline, resembling marble, from near Keeler, California. VI, greyish-white, crumbly, and saccharoidal, from the Binnenthal, Switzerland. VII, hard, compact, from Gerolstein, Rhine. VIII, light colour with pearly lustre, from Costa da Val, Tyrol; $2CaCO_3,MgCO_3,FeCO_3$. IX, greyish-white, compact, from New Almadin, California. X, light grey, granular, and porous, from Raible, Carinthia. XI, grey, large crystals, from Brewster's, New York. XII, *a*, outer layer of pale pink crystals, *b*, inner portion of dark grey crystals. XIII, grey from 'The Dolomites,' Tyrol. XIV, from the Brenner Pass.

	$CaCO_3$.	$MgCO_3$.	Fe_2O_3.	Al_2O_3.	SiO_2.	Total.	Sp. gr.
I.	*51·97*	*37·40*	*0·20*	*Trace*	*10·61*	*100·18*	*2·93*
II.	57·59	24·98	16·05	0·87	0·56	100·05	2·88
III.	87·88	11·85	0·09	—	0·06	99·88	2·57
IV.	27·04	67·91	3·71	0·73	0·13	99·52	2·9
V.	66·08	1·15	0·06	—	32·57	99·86	2·7
VI.	*49·00*	*40·23*	*0·48*	—	*10·84*	*100·55*	*2·85*
VII.	52·93	44·33	0·80	0·22	1·23	99·51	2·82
VIII.	*49·59*	*24·50*	*2·36*	—	*0·12*	*100·01**	*3·01*
IX.	53·28	45·18	8·57	—	0·4	100·11 ?	2·8
X.	54·64	45·18	Trace	0·28	0·23	100·33	2·7
XI.	59·98	36·83	2·44	—	0·33	99·58	2·9
XII*a*.	56·63	41·37	1·18	0·63	0·23	100·04	—
XII*b*.	57·18	36·83	0·89	1·16	3·96	100·02	—
XIII.	94·21	4·15	0·56	0·57	0·48	99·97	2·73
XIV.	96·25	2·98	0·50		0·35	100·08	—

* Including $FeCO_3$, 23·44.

L. J. S.

Analytical Chemistry.

Application of the Interferometer to Gas Analysis. J. D. EDWARDS (*Chem. and Met. Eng.*, 1919, **21**, 560—565).—The gas interferometer measures the difference in refractivity of two gases of binary mixtures. Usually, one of the components is taken as the standard gas, and the difference in refractivity of the mixture and one of its components is determined. For a change of a% of one of the components the change in refractivity

$$\Delta R = 273/T \,.\, p/760 \,.\, a/100(R_1 - R_2).$$

Each scale division corresponds with a definite value of Δr, which is the difference in refraction of the two gases. The calibration of the instrument is described (see also A., 1918, ii, 47). In measuring a small percentage of a gas which deviates appreciably from Boyle's law, a correction is necessitated, as the refractivity of the gas at a low partial pressure differs from the value calculated from the pressure ratios.

In taking readings, calibration curves should be drawn for different temperature and pressure intervals from which readings may be taken by interpolation. A variation of 3° in the temperatures of estimation and of calibration involves an error of 1%. The error due to shifting of the central white or achromatic fringe was investigated by Adams (A., 1915, ii, 478).

Typical illustrations are given of the use of the instrument for air–carbon dioxide mixtures. It may also be employed for the analysis of flue gases and the determination of helium in mixtures.

A table is given showing the relative sensitiveness of the interferometer for different gases. W. J. W.

Improved Orsat Apparatus for Gas Analysis. G. W. Jones and F. R. Neumeister (*Chem. and Min. Eng.*, 1919, **21**, 734—736).—*The modification of Orsat's apparatus used by the* Bureau of Mines, U.S.A., has a Jager's copper oxide tube for the removal of hydrogen and carbon monoxide. The gas burette can be put in communication either with the Orsat pipettes, containing the usual reagents for carbon dioxide, unsaturated hydrocarbons, and oxygen, or with a compensator of the Peterssen type, the mercury in which forms contact with a platinum wire and lights a lamp, when the levelling bulb is raised or lowered, and thus facilitates the reading of the level. The copper oxide tube above the Orsat bulbs is heated by means of an electrical heater, which is lowered over it, and then rests on supports. For the determination of hydrocarbons in a gas, a combustion is made in the combustion pipette with a measured quantity of oxygen, the pipette being cooled by compressed air to prevent breakage, and the amounts of the two predominating hydrocarbons are calculated by means of the usual formulæ from the total contraction and amount of carbon dioxide found after the combustion. [See, further, *J. Soc. Chem. Ind.*, 1920, 138A.] C. A. M.

Theory of Electrometric Titration. W. D. Treadwell (*Helv. Chim. Acta*, 1919, **2**, 672—680).—A theoretical paper in which the determination of the end-point in the titration of silver solutions is considered. The method consists in measuring the terminal voltage between a standard silver chloride cell and a silver electrode immersed in the solution, the end-point being that at which the voltage becomes zero. The theory is considered for the titration of solutions of pure silver salts and of the case where there is a quantity of other substances present. J. F. S.

Electrometric Titration. W. D. Treadwell and L. Weiss (*Helv. Chim. Acta*, 1919, **2**, 680—697).—It is shown that the end-

point of many titrations may be determined electrometrically by measuring the terminal voltage between a metal electrode, which is immersed in the solution being titrated, and is capable of sending the same ions into the solution, and a comparison electrode made of the same metal and the insoluble precipitate or product produced *in the titration*. The two terminals are directly connected with a voltmeter, and the point of zero potential is the end-point of the titration, that is, the point at which the concentration of the metal ions is the same in both the solution being titrated and the comparison electrode. It is essential that during the titration the liquid should be rapidly stirred, and the authors describe an apparatus in which the comparison electrode is built up in the stirrer. In the case of silver solutions, the comparison electrode is Ag | AgCl sat.||, a silver wire furnishes the electrode in the solution, and the titration is carried out with standard sodium chloride. The results are extraordinarily good. In the presence of foreign substances the titration values are too low, but they may be corrected from the course of the titration curve. Hydrogen sulphide may be *titrated with silver ions, using as comparison electrode the combination* Ag | Ag_2S . dil. $NaNO_3$||. Mercurous ions may be titrated by chloride ions, using as comparison electrode

$$Pt . Ag | Hg_2Cl_2 \text{ dil. } H_2SO_4||,$$

and a *similar* silver-plated platinum wire as titration electrode. *Better results are obtained if the titration is carried out with* bromide ions and the calomel in the comparison electrode substituted by mercurous bromide. Copper ions may be titrated by ammonium thiocyanate, using as comparison electrode

$$Cu | CuCNS . \text{dil. } NaHSO_3 ||.$$

In the foregoing cases soluble electrodes have been employed; further experiments were made with insoluble electrodes, and it is found that zinc ions may be titrated with ferrocyanide ion, using as titration electrode a platinum gauze and as comparison electrode Pt | $Zn_2Fe(CN)_6$. HCl(5 c.c. in $300H_2O$)||. The titration in this case is carried out at 70°. Ferrous chloride may be titrated with potassium dichromate, using an already completed titration as the comparison electrode and platinum wires in both solutions. This titration is also carried out in warm solutions. Uranous ions may be titrated with potassium permanganate in warm solution, using platinum wires and a uranyl solution as the comparison electrode. Vanadyl solutions may be similarly titrated with permanganate, using platinum wires and a vanadate solution as comparison electrode. In the case of the hydrogen-ion titration, the electrode is too slow in its action for the method as at present constituted to give sharp results. J. F. S.

Electrometric Titration. J. Pinkhof (*Chem. Weekblad*, 1919, **16**, 1163—1167).—The investigation concerned the selection of a constant electrode which should have the same potential as the electrode of the liquid at the moment when the end-point was reached. It would then be merely necessary to determine whether the difference of potential of the two electrodes was positive or nega-

tive. To ascertain which compensation electrode is suitable, a potential measurement was made during titration, and when the desired potential was found a combination of electrode and liquid was sought which would give this potential. For the titration of halogens in presence of each other, *N*-potassium bromide is suitable for the compensation electrode in the estimation of the iodine. For the bromine Ag–AgCl–0·2*N*Cl is used. In titrating heavy metals with sodium sulphide, a silver-halogen compensation electrode is employed. Titrations of bases with mercuric oxide electrode and the use of the hydrogen electrode are discussed. W. J. W.

A Rapid Hydrogen Electrode Method for Determination of Hydrogen-ion Concentrations in Bacterial Cultures or in other Turbid or Coloured Fluids. HARRY M. JONES (*J. Infect. Dis.*, 1919, **25**, 262—268).—As compared with the colorimetric method, the apparatus described has wider application, is more accurate, less cumbersome, and only slightly less rapid. The hydrogen electrode vessel described was designed to provide a vessel accurate at least to 0·01 p_H and to give a rapid saturation with hydrogen gas, and yet one which is easily constructed. A rapid and labour-saving technique combining the indicator and the gas-chain methods is described, which obviates the difficult task of preparing standard solution for the former method, and of making needless repetitions by the latter. CHEMICAL ABSTRACTS.

Iodometric Estimation of Acids. I. M. KOLTHOFF (*Pharm. Weekblad*, 1920, **57**, 53—68).—The author has investigated the iodometric method, especially with reference to weak acids. The influence of dilution in the case of strong acids, of catalysts, and of a variation in the amount of potassium iodide added, was determined. Tests were carried out with hydrogen chloride, tartaric acid, citric acid, lactic acid, malic acid, succinic acid, acetic acid, formic acid, benzoic acid, salicylic acid, sodium phosphate, and currant juice. The iodometric method gives excellent results with strong acids, especially if diluted, in which case the reagents, after mixing, must remain for ten minutes before titration. A deficiency of potassium iodide causes inaccuracy. Organic oxy-acids can be accurately estimated if a salt of calcium, magnesium, or zinc is added. For phosphoric acid and weak organic acids, not containing a hydroxy-group, the method is unsuitable, but it may be used in the case of formic acid. The applicability of the method to the estimation of fruit juices requires further investigation. W. J. W.

Indirect Electrolytic Estimation of Anions without Platinum Electrodes. II. E. LASALA (*Anal. Fis. Quim.*, 1919, **17**, 235—247).—A continuation of work already published (A., 1919, ii, 239). The present communication deals also with anions which form insoluble silver salts. These are carbonate, oxalate, ferro- and ferri-cyanide, orthophosphate, arsenate, chromate, and thiocyanate. The anion is precipitated as insoluble silver salt.

This is dissolved in a suitable solvent, and the silver estimated electrolytically with a nickel-plated copper cathode and an iron anode. Satisfactory results were obtained only in the case of carbonate, oxalate, ferro- and ferri-cyanide, and thiocyanate. The method was applied to the separation of chloride and iodide. The precipitated mixed silver haloid is washed with ammonia solution (D 0·92). The silver chloride is electrolysed after the addition of ammonium sulphate. The residual iodide is dissolved in 20% solution of potassium cyanide and electrolysed. A small correction must be applied for the solubility of silver iodide in ammonia solution. W. S. M.

Electrolytic Estimation of the Halogens. An Indirect Method. J. H. REEDY (*J. Amer. Chem. Soc.*, 1919, **41**, 1898—1902).—The decomposition voltage of *N*-sulphuric acid, saturated with silver chloride, between silver coated with silver chloride as anode and bright platinum as cathode is found to be 0·59 volt, which corresponds exactly with the sum of the solution potential of silver (0·52 volt) and the overvoltage of hydrogen on bright platinum (0·07 volt). As long as this limiting voltage of 0·59 volt is not exceeded, the electrolysis of haloid solutions with silver anodes proceeds with the formation of an adherent layer of silver haloid on the anode without precipitation in the solution. With the completion of the deposition of the halogen, silver ions appear in the solution with no break in the continuity of the current and with scarcely any rise in potential. An indirect method of estimation of chlorides, bromides, and iodides is based on the above facts. The principle of the method consists in depositing the halogen on a silver anode under a constant voltage of 0·59 volt; some silver will thereby be lost from the anode. The anode is then dried and weighed, and the silver haloid is reduced to metallic silver and the loss in weight determined, which gives the weight of the halogen. A lead accumulator of large capacity is connected across the ends of a sliding rheostat and a current of *E.M.F.* 0·59 volt tapped off. The electrolysis vessel consists of a beaker of 400 c.c. capacity fitted with an anode of silver gauze, coated with silver electrolytically, and a bright platinum cathode and a stirrer. The electrolysis is carried out with 200 c.c. of solution for about fifteen minutes; the current flowing at first is rather large, but after about fifteen minutes it becomes negligible. The potential is then raised to 0·60 volt for five minutes. The silver electrode with its halogen deposit is washed, dried, and weighed. After weighing, it is made the cathode in a dilute solution of sodium hydroxide and electrolysis carried out until hydrogen is freely liberated from the surface. The silver haloid is thus reduced to black silver, which is not very adherent and must be carefully handled. After a thorough washing, the electrode is heated at 500° in an electric furnace until the deposit is white, and thoroughly sintered together. It is then weighed, and the loss in weight gives the weight of the halogen. The results given in the paper show that the method is quite as good as the usual gravimetric method.

J. F. S.

Estimation of Bromide in Mineral Waters and Brines. W. W. SKINNER and W. F. BAUGHMAN (*Science*, 1919, **50**, 50).—Chromic acid in concentrated solution liberates bromine quantitatively from bromides at the ordinary temperature, and the bromine is removed by aspiration. Only a trace of chlorine is liberated from chlorides. When chromic acid acts on a solution containing chloride and bromide, therefore, the mixture of halogens removed by aspiration is dissolved in a solution of sodium sulphite and hydroxide, which is then evaporated to dryness and the residue again treated with chromic acid solution and aspirated a second time. The double treatment gives very trustworthy results.

CHEMICAL ABSTRACTS.

Estimation of Alkali Sulphide in Dilute Solution. H. G. BENNETT and W. G. BENNETT (*J. Soc. Leather Trades Chem.*, 1919, **3**, (11), 190—193).—A measured quantity of the solution containing not more than 0·04% of hydrogen sulphide is distilled in an atmosphere of carbon dioxide with an excess of boiling magnesium chloride solution. A current of carbon dioxide carries the liberated hydrogen sulphide into a receiver containing standard iodine solution. A second receiver, containing standard sodium arsenite solution, is arranged to trap any iodine vapour carried over by the gas. The method is accurate under these conditions and provided there are no rubber connections exposed to the iodine vapour. D. W.

Neutralisation Curve of Sulphurous Acid. I. M. KOLTHOFF (*Chem. Weekblad*, 1919, **16**, 1154—1163).—The accuracy of the results when sulphurous acid is titrated with methyl-orange or dimethyl-yellow as indicator depends on the concentration of the hydrogen ions of the sodium hydrogen sulphite, and therefore also on the second dissociation constant of the sulphurous acid. This has been determined from the degree of hydrolysis of solutions of sodium sulphite and found to be 1×10^{-7} at 15°. The hydrogen-ions concentration of a 0·1 mol. sodium hydrogen sulphite solution calculated from the two dissociation constants gave the value $[H^{\cdot}] = 3{\cdot}3 \times 10^{-5}$. A curve showing the neutralisation of sulphurous acid was constructed. In the titration of sulphurous acid errors of ±2% and of ±6% were obtained when the indicators were dimethyl-yellow and phenolphthalein respectively. The addition of sodium chloride reduced the error with phenolphthalein to ±2%. Accuracy can only be ensured if excess of barium nitrate is added after the pink coloration of the phenolphthalein has appeared, and the titration then continued to the end-point. W. J. W.

Estimation of Sulphates in the presence of Organic Sulphonic Acids. T. CALLAN, JAS. A. RUSSELL HENDERSON, and R. BARTON (*J. Soc. Chem. Ind.*, 1919, **38**, 410—411T).—The solution of the substance (containing about 0·2 gram of sulphate) is rendered slightly ammoniacal (a small quantity of calcium chloride is also added to precipitate any carbonate, which is then separated by filtration), and the mixture is boiled until all excess of ammonia

has been expelled. Twenty c.c. of $N/4$-barium chloride solution are then added, the heating continued for a few minutes, and the excess of barium titrated with $N/4$-potassium chromate solution, using starch-iodide paper as indicator. A drop of the mixture is placed on the paper, and the edge of the spot is touched with a drop of very dilute hydrochloric acid. A blue colour develops in about ten seconds when an excess of soluble chromate is present. An immediate blue colour indicates that a considerable excess of chromate has been added. W. P. S.

Detection of Nitrogen in Organic Compounds by Castellana's Reaction. J. FLIERINGA (*Pharm. Weekblad*, 1920, **57**, 3—4).—Castellana's reaction (A., 1905, ii, 207) may give a positive reaction even in nitrogen-free compounds, owing to combination of atmospheric nitrogen, if the magnesium is in excess. It is preferable to use a mixture of 2 parts of sodium carbonate and 1 part of magnesium. Sodium carbonate containing 1 molecule of H_2O should be employed. Addition of sugar to the reaction mixture eliminates the error caused by absorption of atmospheric nitrogen. W. J. W.

The Relative Accuracy of Colorimetric and Titrimetric Procedures for estimating Nitrogen as Ammonia. E. R. ALLEN and B. S. DAVISSON (*J. Biol. Chem.*, 1919, **40**, 183—197).—It appears that the colorimetric methods are slightly the more accurate. On the other hand, the conditions for accurate titrations may be attained more easily than those for satisfactory Nessler estimations, and at the same time the titrimetric methods are applicable to a wide range of nitrogen values. The chief disadvantage of the Nessler process is the fact that the reaction is imperfectly understood, and the appearance of clouds and precipitates difficult to avoid. Again, it is believed that the personal error is greater in colorimetric methods than in titrimetric methods. The general conclusion is therefore in favour of the titrimetric methods.

J. C. D.

Estimation of Nitrogen in Nitrates. F. PILZ (*Zeitsch. landw. Vers.-Wesen Deutschösterr.*, 1919, **22**, 180—188; from *Chem. Zentr.*, 1919, iv, 767).—Comparative estimations of nitrogen in nitrates by various methods showed that reduction with Devarda's alloy yielded the most trustworthy results, and is to be recommended more than the method described by Arnd (A., 1917, ii, 504). Busch's method (A., 1905, ii, 418) is less trustworthy. Other methods investigated were the one proposed by Ulsch (reduction in acid solution with iron powder) and the indirect method (conversion of the nitrate into chloride). W. P. S.

Method for the Estimation of Minute Quantities of Nitrogen in Organic Substances, which furnishes a New Quantitative Method of Diagnosis in some cases of Mental Disease. R. V. STANFORD (*Rep. Chem. Lab. Cardiff City Mental Hospt.*, 1919, No. 2. Compare A., 1913, i, 930).—A small quantity

of the organic substance, as, for example, 1 c.c. of cerebrospinal fluid, is oxidised by the Kjeldahl process in the usual manner. The subsequent distillation is carried out in the ordinary apparatus, but the distillate is collected in three fractions in Nessler cylinders. The third fraction should show little or no coloration with Nessler's reagent. The colour produced by the first two fractions is compared in the usual manner with that produced by a standard solution of ammonium chloride. Considerable care has to be taken to avoid errors arising from ammonia in the reagents and apparatus.

The author records a number of analyses of cerebrospinal fluid from mental cases. The "nitrogen number," that is, the number of hundredths of a milligram of total nitrogen contained in 1 c.c. of cerebrospinal fluid, may be of value in diagnosis. On the whole, density and nitrogen number of the fluids run parallel to one another.

No traces of choline and only the merest traces of ammonium salt were detected in the cerebrospinal fluid in mental disease.

J. C. D.

Process for the Estimation of Arsenic. Chemistry of the Marsh-Berzelius Process. B. S. EVANS (*Analyst*, 1920, **45**, 8—17).—The arsenic is evolved as hydrogen arsenide, in the same way as in the ordinary Marsh-Berzelius test, but is conducted over a roll of red-hot copper, which retains the arsenic, the amount of which is obtained from the increased weight of the copper. The compound formed with the copper usually melts and resembles solder in appearance, but occasionally brilliant, silvery-white, blade-shaped crystals are produced. Analyses of the deposits gave 67·5 and 70·5% of copper and 32·28 and 29·27% of arsenic, and thus appeared to be mixtures of the arsenides Cu_3As and Cu_5As_2. The results obtained with elementary arsenic and various arsenic compounds were invariably 1·4% too low, and the cause of this loss could not be definitely traced, although the results indicated that if the arsenic remained in the flask, it was in the form of a very stable complex. In order to prevent separation of elementary arsenic, it is advisable that the amount of substance introduced should contain considerably less than 0·5 gram of arsenic. [See also *J. Soc. Chem. Ind.*, 1920, February.] C. A. M.

Estimation of Arsenic in Tin and Tinnings. LUCIEN VALLERY (*Compt. rend.*, 1919, **169**, 1400—1402).—Marsh's method is liable to give results which may, in some cases, be wrong to the extent of 75% of the amount found when applied to the estimation of arsenic in tin. The author recommends that the arsenic should be distilled off as arsenic chloride by Hollard and Bertiaux's method, and the arsenic estimated colorimetrically in the distillate after reduction to colloidal arsenic by means of hypophosphorous acid. In this way, the results obtained are accurate to within 3% of the total at a concentration of 1 in 100,000. W. G.

New Method of Estimation of Carbon and Hydrogen in Organic Substances. Kunihiko Sumikura (*J. Tokyo Chem. Soc.*, 1919, **40**, 593—606).—The essential point of the method is the combined use of platinum and cerium dioxide. (1) *Substances containing Carbon, Hydrogen (and Oxygen) only.*—An ordinary combustion tube is filled, in order, with cerium dioxide (5 cm.), porcelain boat, cerium dioxide (8 cm.) (only one burner is necessary under each of these), and a coil of platinum or platinum-iridium wire (2 m.), which is electrically heated with adjustable resistances. The wire is first heated in a separate tube before being placed in the combustion tube. The cerium dioxide is prepared by heating copper gauze packed with asbestos soaked in a solution of ceric nitrate.

(2) *Substances containing Nitrogen and Sulphur.*—Lead dioxide is placed between the second cerium dioxide gauze and the platinum coil, and is heated at 300—350°. (3) *Substances containing Halogens.*—Silver foil is placed between the second cerium dioxide gauze and the platinum wire. If nitrogen is also present, lead dioxide is placed between the silver foil and the platinum wire, and is heated at 300—320°. (4) *Substances containing Phosphorus.*—Lead monoxide is mixed with the substance. Trustworthy results are recorded. Chemical Abstracts.

Rapid Estimation of Carbon Monoxide in Air. Arthur B. Lamb and Alfred T. Larson (*J. Amer. Chem. Soc.*, 1919, **41**, 1908—1920).—Two methods for the rapid estimation of small quantities of carbon monoxide in air are described. In the first method, the gas is passed over a platinum wire heated to redness, and the carbon monoxide partly burned in contact with it. The gas then passes over heated copper oxide, where the carbon monoxide is completely burnt; it then passes through a spiral contained in a thermostat to bring it to its original temperature, and finally over a second exactly similar platinum wire heated by the same current as the first. The two platinum wires are made arms of a Wheatstone bridge, and since the first wire will necessarily be hotter than the second, they will have different resistances. The change in the resistance of the first wire gives a measure of the carbon monoxide concentration. In the second method, the mixture is passed through a platinised platinum catalyst, when the carbon monoxide is completely burnt. The temperature change is measured by a thermo-element, and indicates the concentration of carbon monoxide. Both methods are rapid, and the latter is particularly accurate, easy to instal and to operate. The catalyst, with reasonable precautions, remains active for many weeks.

J. F. S.

Apparatus for the Volumetric Estimation of Small Quantities of Carbon Dioxide by Displacement from Liquids by means of a Rapid Current of Air at the Ordinary Temperature and Pressure. A. Costantino (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 118—121).—In the apparatus described, which

consists of a closed system, a rotary mineral oil pump causes the repeated circulation of purified air, first through the liquid containing the carbon dioxide, and then through a definite volume of standard barium hydroxide solution, this being subsequently titrated with acid in presence of phenolphthalein. The determination occupies in all about forty-five minutes. Test experiments with sodium carbonate solutions containing 6·4—21 mg. of carbon dioxide show that the method yields accurate results. T. H. P.

Estimation of Metals by Electrolytic Deposition without using an External Supply of Electricity. MAURICE FRANÇOIS (*Ann. Chim.*, 1919, [ix], **12**, 178—192).—A more detailed account of work already published (see A., 1919, ii, 34). W. G.

Use of Nickel Crucibles for the J. Lawrence Smith Method in Estimating Soil Potassium. SETH S. WALKER (*J. Ind. Eng. Chem.*, 1919, **11**, 1139—1140).—The same results are obtained whether platinum or nickel crucibles are used for the heating of the soil with ammonium chloride and calcium carbonate, but the nickel crucible is attacked by the mixture and the life of the crucible is short. W. P. S.

The McCrudden Gravimetric Calcium Method Modified. J. P. HALVERSON and J. A. SCHULZ (*J. Ind. Eng. Chem.*, 1920, **12**, 77—78).—The calcium oxalate precipitate is collected on a filter of specially prepared asbestos contained in a Gooch crucible; after washing, both filter and precipitate are mixed with water, acidified with sulphuric acid, and titrated at 65° with permanganate solution. The filter is prepared by digesting ignited asbestos with dilute sulphuric acid and a slight excess of permanganate for one hour at 60° to 70°, and then washing it until free from acid. [See, further, *J. Soc. Chem. Ind.*, 1920, February.] W. P. S.

Estimation of the Calcium Oxide Content of Milk of Lime. GEORG LENART (*Zeitsch. Ver. deut. Zuckerind.*, 1919, 1—15, 360—361).—Mategček's table (*Österr.-Ungar. Zeitsch. Zuckerind.*, 1871, **12**, 718) correlating the sp. gr. and calcium oxide content of milk of lime is regarded as far from correct, whilst that published by Lunge and Blattner (*Dingl. Polytechn. J.*, 1883, 466) is also considered to be untrustworthy. Experiments are described demonstrating the difficulty of obtaining exact results by means of the hydrometer (the method of density determination adopted in the construction of the second table), since the readings are influenced by the shape and length of the spindle, by the width and depth of the column of liquid in the cylinder, and also by the degree of movement imparted to the liquid at the moment of observation. Using a pyknometer consisting simply of a cylindrical vessel having a capacity of about 500 c.c., provided with a ground-glass plate as cover, a new table has been constructed by the author in which the density values range from 1·0085 to 1·2195 (1·5° to 26·2° Bé.)

at 20°, temperature corrections being stated for readings mad between 20° and 40°. Milk of lime which has been vigorousl shaken for about two hours assumes a viscous condition, in whic the particles remain almost completely in suspension for som days, this being believed to be due to the formation of a hydrate compound, probably $Ca(OH)_2,H_2O$, to which attention has alread been directed by Herzfeld (*Zeitsch. Ver. deut. Zuckerind.*, 1897 817) and by Karcz (*Chem. Zeit.*, 1898, **22**, 38). J. P. O.

The Permanganate Method for Copper. Louis F. Clar (*J. Ind. Eng. Chem.*, 1919, **11**, 1138—1139).—A modification o the procedure for the titration of cuprous thiocyanate with per manganate solution is proposed, with the object of making th estimation less arbitrary. The cuprous thiocyanate precipitate i treated in a beaker with 25 c.c. of hot 4% sodium hydroxide solu tion until the precipitate is decomposed, 25 c.c. of cold 15% sulphuric acid and a quantity of 1% ferric sulphate (anhydrous salt solution are added, and the mixture is titrated with permanganat solution. Towards the end of the titration, and when the mixtur becomes whiter in colour, 5 c.c. of concentrated hydrochloric aci are added, and the titration then completed. Under these con ditions, 6 atoms of copper should be equivalent to 7 atoms of iron or a ratio factor of 0·1626; the ratio factor actually found as th result of experiment is 0·1646. [See, further, *J. Soc. Chem. Ind.* 1920, 138A.] W. P. S.

Microchemical Identification of Soluble and Insolubl Mercury Compounds. G. Denigès (*Bull. Soc. Pharm. Bordeaux* 1919; from *Ann. Chim. anal.*, 1919, [ii], **1**, 383—385).—The test depend on the characteristic crystals obtained when a small quantity of the compound is treated with a drop of potassium bromide-iodide solution. Mercurous compounds and mercuric cyanide are oxidised previously with bromine. Mercuric iodide itself is identified by the crystals obtained from its alcohol or acetone solution. W. P. S.

Volumetric Estimation of Mercuric Chloride. Otto Sasse (*Pharm. Zeit.*, 1919, **64**, 633).—Referring to the method described by Utz (A., 1919, ii, 428), the author mentions that he himsel had published a method (*Pharm. Zeit.*, 1887) for the volumetric estimation of mercuric chloride; this method depends on a titration with potassium iodide solution, and is trustworthy.

W. P. S.

Application of Rotating Reductors in the Estimation of Iron. Walter Scott (*J. Ind. Eng. Chem.*, 1919, **11**, 1135—1137). —Gooch and the author have shown previously (A., 1918, ii, 373) that vanadic acid may be reduced by rapidly rotating anodes of silver or copper, and the author now describes a similar method of reduction for ferric salts. The latter in sulphuric acid solution are reduced completely by rotating reductors of zinc or aluminium, with or without the use of an external current. W. P. S.

A Sensitive Reaction for Manganese. P. H. Hermans (*Pharm. Weekblad*, 1919, **56**, 1344—1346).—Caron and Raquet's reaction for manganese (*Rép. Pharm.*, 1919, 97) was independently discovered by the author, and was, in addition, utilised as a test for nitrogen tetroxide and for nitrites. All oxidising agents are not effective in promoting the red coloration, for example, hydrogen peroxide, potassium persulphate, chlorine, bromine, iodine, chloric acid, iodic acid, potassium ferricyanide, but addition to them of 0·5% solution of osmic acid produces a satisfactory result. Active oxidising agents for the test are bleaching powder, potassium permanganate, and dichromate, lead peroxide, cerium ammonium nitrate, nitrous acid, and nitrogen tetroxide.

Lead peroxide is most suitable for the manganese test. The reaction is sensitive to 0·07 mg. manganese or 0·03 mg. sodium nitrite per c.c. of solution.

The red coloration is considered to be a complex alkali manganese oxalate. W. J. W.

Indirect Detection of Tin. Fr. Feigl (*Chem. Zeit.*, 1919, **43**, 861).—Ferrous salts give a red precipitate with an ammoniacal solution of dimethylglyoxime, but the presence of ferric salts, which give a precipitate of ferric hydroxide with the reagent, interferes with the test. The precipitation of ferric iron as hydroxide and of ferrous iron as ferrous dimethylglyoxime may be prevented by adding an organic hydroxylated compound, such as citric or tartaric acids or potassium sodium tartrate, and the ferrous ion then gives a carmine-red solution. In each case, complex iron compounds are formed. In using this reaction as a sensitive indirect test for tin, the mixed sulphides, presumably of antimony and tin, are dissolved in hydrochloric acid, and one portion of the solution is tested for antimony with iron wire. In a second portion, the tin and antimony are precipitated by means of pure zinc, and the tin extracted from the deposit by means of concentrated hydrochloric acid. The solution is poured into a hot dilute solution of ferric chloride, a little citric acid or potassium sodium tartrate added, and the liquid tested with ammoniacal alcoholic dimethylglyoxime solution. The ferrous ion formed by reduction with the stannous ion will give a red coloration, the intensity of which is proportional to the amount of stannous chloride. C. A. M.

Estimation of Thiophen in Industrial Benzenes. André Meyer (*Compt. rend.*, 1919, **169**, 1402—1404).—A modification of Denigès's method (compare A., 1895, ii, 332, 372). Denigès's reagent is prepared by dissolving 50 grams of mercuric oxide in 200 c.c. of sulphuric acid diluted with 1000 c.c. of water. Twenty c.c. of this reagent are mixed with 75 c.c. of methyl alcohol and 5 c.c. of the benzene under examination in a stoppered bottle. The mixture is shaken from time to time, and, after thirty minutes, is filtered. Ten c.c. of the filtrate are diluted with 20 c.c. of water, a few drops of nitric acid are added, and the whole is titrated with

$N/10$-ammonium thiocyanate solution, using 1 c.c. of a 20% iron ammonium alum solution as indicator. In view of the possible presence of acetone in the methyl alcohol, a blank experiment is conducted, using pure benzene free from thiophen. The difference between the two titrations is a measure of the mercury precipitated by the thiophen as the compound, $(HgO)_2SO_4,HgSC_4H_4$, and the factor for the conversion of mercury to thiophen is 0·14. W. G.

Titration and Partial Reduction of Nitro-compounds with Titanous Chloride. C. F. VAN DUIN (*Chem. Weekblad.* 1919, **16**, 1111—1122).—An examination of the titanous chloride method for the titration of nitro-compounds. The constancy of titre of a titanous chloride solution at the ordinary temperatures and after heating was especially investigated; also the general applicability of the method to various classes of nitro-compounds. At the ordinary temperatures, only slight variations in titre were found after keeping for several days. Titration experiments before and after heating the titanous chloride solution were carried out in comparable conditions in presence of alcohol, hydrochloric acid, and acetic acid. It was found that the assumption of an invariable titre during the heating of the titanous chloride solution led to quite erroneous results. The error is small in presence of acids, especially in hydrochloric acid, tolerable results being only obtained in strongly acid solutions. From experiments with picric acid, *m*-dinitrobenzene, and *s*-trinitrotoluene, the author concludes that the method yields results of the same order of accuracy as the Dumas method. The reduction and titration of the following classes of nitro-compounds were carried out: nitroamines (*s*-trinitrophenylmethylnitroamine, aminotrinitrophenylmethylnitroamine, trinitromethylnitroaminophenol, trinitromethylnitroaminoanisole, trinitrodimethyldinitroaminobenzene), tetranitro-compounds (tetranitrophenol, tetranitrophenylmethylnitroamine, tetranitroaniline), and hexanitro-compounds with two nuclei (hexanitrodiphenyl sulphide, hexanitrodiphenylsulphone). In the reduction of nitroamines, side reactions may take place in which the nitroamino-group is entirely removed from the nucleus. In all cases, blank experiments must be carried out in order to estimate the alteration in the titanous chloride solution on heating. The amount of excess of the solution necessary for complete reduction must also be determined in each case. Only in those conditions can this method of nitrogen analysis be considered superior to that of Dumas.

W. S. M.

Detection of Methyl Alcohol in Ethyl Alcohol. M. POLINSKI (*Chem. Analyst*, 1919, **28**, 11).—Five c.c. of the sample are distilled with 50 c.c. of water and 3 grams of sodium persulphate, the distillate being collected in fractions of 2 c.c. each. The fifth fraction is treated with eight drops of a freshly prepared, filtered 1% solution of phenylhydrazine hydrochloride, four drops of 5%

potassium ferrocyanide, and 1 c.c. of concentrated hydrochloric acid. A pink coloration is produced if methyl alcohol is present.

CHEMICAL ABSTRACTS.

Complex Organic Mercury Compounds. EINAR BIILMANN (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 12, 1—11).—The complex compound formed from allyl alcohol and mercuric acetate is very stable, the concentration of the mercuric ion in a 1/160-molar solution being only $10^{-8 \cdot 40}$ (compare A., 1917, i, 123). This fact can be made use of in the electrometric estimation of allyl alcohol. The aqueous solution of allyl alcohol is put in a beaker containing mercury, which forms one electrode, the other being a calomel electrode. A standard solution of mercuric acetate is then run in, and the *E.M.F.* curve plotted. The point of inflexion on the curve is very sharp, and accurate results are obtained.

Allyl alcohol can also be estimated by adding mercuric acetate and potassium bromide to the solution, and titrating the acetic acid set free, with phenolphthalein as indicator. The liberation of acetic acid is quantitative, according to the equations: $C_3H_5 \cdot OH + Hg(OAc)_2 = C_3H_5 \cdot O \cdot Hg \cdot OAc + AcOH$; $C_3H_5 \cdot O \cdot Hg \cdot OAc + KBr = C_3H_5 \cdot O \cdot HgBr + OAcK$. Mercury can also be estimated very accurately by making use of the quantitative reaction,

$$C_3H_5 \cdot O \cdot Hg \cdot OH + KBr = C_3H_5 \cdot O \cdot HgBr + KOH.$$

A weighed quantity of mercuric oxide is dissolved in 5*N*-sulphuric or nitric acid; the solution is diluted with water free from carbon dioxide, a few c.c. of allyl alcohol added, and then *N*/5-sodium hydroxide until the liquid is alkaline to phenolphthalein. The whole is then exactly neutralised with *N*/5-sulphuric acid, 5 grams of potassium bromide added, and the liquid well shaken to give a solution, the entrance of carbon dioxide being carefully excluded. The liberated alkali is then titrated. Halogen acids must not be present in estimations according to this method.

Maleic and crotonic acids do not give sufficiently stable complexes for estimation by the above methods, but *allo*cinnamic acid gives good results with the mercuric acetate–potassium bromide method. Cinnamic acid also gives mercury complexes, and is to be reported on later.

Mercury can be readily and accurately estimated by a modification of Incze's method (A., 1917, ii, 327). To the solution of the mercuric salt, or of mercuric oxide in nitric or sulphuric acid, is added a large excess of alkali; the whole is then exactly neutralised with standard acid, using phenolphthalein as indicator. Potassium iodide (5 grams) is then added, and the liberated alkali carefully titrated, carbon dioxide being excluded. T. S. P.

Titration of Organic Acids in Urine. D. D. VAN SLYKE and W. W. PALMER (*Proc. Soc. Exp. Biol. Med.*, 1919, **16**, 140—141).—Carbonates and phosphates are removed by adding 2 grams of calcium hydroxide to 100 c.c. of urine and filtering after ten minutes. The acidity of 25 c.c. of the filtrate is brought to $p_H = 8$

(circa) by adding 0·2N-hydrochloric acid until the pink colour of phenolphthalein disappears, 5 c.c. of 0·02% Tropœolin OO are added, and the solution is titrated to $p_H = 2·7$ with 0·2N-hydrochloric acid, the volume being brought to approximately 50 c.c. by the addition of water towards the end of the titration. The colour is compared with that of 50 c.c. of a control solution with the same p_H value and indicator. The amount of 0·2N-hydrochloric acid required to give the end-point with a control in which water replaces urine is subtracted. The titration estimates from 93% to 100% of each of the organic acids known to be present in urine in quantitatively significant amounts. It also includes very weak bases, but of this class of substances only creatine and creatinine, which are estimated to nearly 100%, are significant. The titration figure, corrected for the amounts of these two bases, represents the organic acids in urine. CHEMICAL ABSTRACTS.

Detection of β-Hydroxybutyric Acid, Acetoacetic Acid, and Acetone in Urine. R. LILLIG (*Pharm. Zeit.*, 1919, **64**, 696—697, 707—709).—A collection of some sixty methods which have been proposed for the purpose; a brief description is given of each method. W. P. S.

Bellier's Reaction for Vegetable Oils. A. VAN RAALTE (*Chem. Weekblad*, 1919, **16**, 959—960).—The benzene used for this reagent must be free from thiophen, otherwise a dirty green, instead of a violet, coloration is obtained. W. J. W.

Relative Sensitiveness of the Fehling, Phenylhydrazine, and Nylander Tests for the Detection of Dextrose in Urine. GEORGE E. ÉWE (*Amer. J. Pharm.*, 1919, **91**, 717—719).—Fehling's test is the most sensitive of the three tests investigated; it yields a reaction with a solution containing 0·00125% of dextrose. The phenylhydrazine test is also sensitive, giving a reaction, after two hours, with a 0·0025% solution of dextrose, but the Nylander reagent (potassium sodium tartrate, 4 grams; 10% sodium hydroxide solution, 100 c.c.; bismuth subnitrate, 2 grams) fails to give a reaction unless the solution contains at least 0·5% of dextrose. W. P. S.

Titration of Sugars. E. SCHOWALTER (*Zeitsch. Nahr. Genussm.* 1919, **38**, 221—227).—A reply to Rupp and Lehmann (A., 1919, ii, 434); the author maintains the correctness of his former remarks (A., 1919, ii, 172). W. P. S.

The Isaacson Method for Estimating Dextrose. ELISABETTA C. PENNELL (*J. Lab. Clin. Med.*, 1919, **4**, 736—737).—Isaacson's method (A., 1918, ii, 246) was found highly untrustworthy when compared with the Fehling volumetric method.

CHEMICAL ABSTRACTS.

Separation of Dextrose and Lævulose. FRANZ LUCIUS (*Zeitsch. Nahr. Genussm.*, 1919, **38**, 177—185).—A method for the estimation of dextrose in the presence of lævulose depends on the fact that the rotation of the latter is destroyed by heating for seven

ours with dilute hydrochloric acid, whilst that of dextrose is not ffected. Fifty c.c. of the sugar solution (containing from 2 to 4% of the sugars) are mixed with 10 c.c. of 5*N*-hydrochloric acid and eated in a boiling water-bath for seven hours. The mixture is hen nearly neutralised with sodium hydroxide solution, diluted to 00 c.c., treated with animal charcoal and filtered, if necessary, and olarised at 20°. About 99% of the dextrose actually present is ound. The dextrose remaining after the acid treatment cannot be stimated by determining the copper-reducing power of the solution s the lævulose is converted into reducing substances, which, howver, are optically inactive. W. P. S.

Separation of "Saccharin" from Benzoic Acid. E. SCHOWALTER (*Zeitsch. Nahr. Genussm.*, 1919, **38**, 185—194).—The resence of "saccharin" interferes with the estimation of benzoic cid in foods, etc., by the methods described by Mohler, von der Heide, and Grossfeld (A., 1908, ii, 906; 1910, ii, 359; 1915, ii, 848), ut the two substances may be separated from one another by aking advantage of the insolubility of "saccharin" in carbon tetrahloride. The residue obtained on evaporating the ethereal soluion of the two substances at a low temperature is dried under educed pressure to remove the last traces of ether and acetic acid, nd is then treated with carbon tetrachloride; the benzoic acid disolved by this solvent may be estimated by titration and the nsoluble "saccharin" identified by Klostermann and Scholta's reacion (A., 1916, ii, 586). Separation of the two substances between ublimation is untrustworthy; "saccharin" begins to sublime at 20° and 130°. Animal charcoal absorbs considerable quantities of saccharin," its anhydride and sodium salt, as well as benzoic acid nd benzoates, from an aqueous solution. W. P. S.

Estimation of *p*-Phenylenediamine. T. CALLAN and JAS. A. RUSSELL HENDERSON (*J. Soc. Chem. Ind.*, 1919, **38**, 408—410T).—A modification of a method described by Effront (A., 1905, ii, 60) s recommended. Fifty c.c. of sodium hypochlorite solution, conaining 12—15% of available chlorine, are diluted to 1 litre, and 00 c.c. of this solution are diluted with an equal volume of water, gram of sodium carbonate is added, followed by 10 c.c. of the -phenylenediamine solution (in dilute hydrochloric acid); the latter olution should contain from 2 to 6% of the substance, and the addiion should be made gradually with constant stirring. Benzouinonedichloroimide is precipitated as a white substance and, withut filtration, the excess of chlorine in the mixture is titrated with *N*/10-sodium arsenite solution. The difference between this titraion and the quantity of arsenite solution required for the titration f the hypochlorite solution itself is equivalent to the amount of hlorine removed from solution as dichloroimide; 1 c.c. of *N*/10-arsenite solution therefore corresponds with 0·0018 gram of -phenylenediamine. The method may also be used for the estimaion of *p*-nitroaniline, *p*-aminodiphenylamine, benzidine, and naphthylene-1:4-diamine, but with the latter the yield found is

only 98—99% of the quantity of substance present owing to the slight solubility of the dichloroimide formed. The method is not applicable to substances containing a sulphonic group, since these give soluble dichloroimides. W. P. S.

Estimation of Carbamide in Blood and Urine. H. Citron (*Deut. med. Woch.*, 1919, **45**, 975; from *Chem. Zentr.*, 1919, iv, 719).—A reply to Brahm (this vol., ii, 66). H. W.

Electrometric Method for the Estimation of Ferrocyanides depending on a Change in Oxidation Potential. G. L. Kelley and R. T. Bohn (*J. Amer. Chem. Soc.*, 1919, **41**, 1776—1783).—Solutions of ferrocyanides may be estimated by titration with potassium permanganate in the presence of sulphuric acid, using the sudden change in *E.M.F.* observed with a bright platinum electrode to mark the end-point. The method is as follows: About 1 gram of potassium ferrocyanide in 250 c.c. of water and 2·5—5·0 c.c. of sulphuric acid (D 1·58) is titrated with 0·05*N*-potassium permanganate, *using an electrometric apparatus* which will indicate changes of potential of the order of one millivolt (A., 1917, ii, 512). A small precipitate may form during the titration, but this will redissolve. The titration should be performed slowly with mechanical stirring. As the end-point is approached the permanganate should be added drop by drop, and time allowed for the completion of the reaction. The end-point is taken as the point of greatest change in potential for equal additions of permanganate. Should too much permanganate be added, the end-point may be approached from the other side by adding a standard solution of ferrocyanide. The presence of ferricyanides does not interfere with the titration, neither do amounts of chloride up to 1 gram of sodium chloride. Any salts which under the conditions of experiment produce a precipitate with either ferrocyanide or ferricyanide seriously interfere with the method. J. F. S.

Use of Silicotungstic Acid in the Estimation of Alkaloids. Erwin Taigner (*Zeitsch. anal. Chem.*, 1919, **58**, 346—352).—Silicotungstic acid solution may be used for the quantitative precipitation of atropine, strychnine, and cocaine from their hydrochloric acid solutions; the precipitates formed are collected, after the addition of *sodium chloride*, washed with *1% hydrochloric acid*, dried at 40°, and weighed. The precipitates have the general formula $12WO_3,SiO_2,2H_2O,4$-alkaloid. W. P. S.

Colour Reactions of Emetine. Abel Labille (*Arch. méd. exp.*, **27**, 296; *Zentr. Biochem. Biophys.*, 1919, **20**, 398).—Emetine hydrochloride develops a yellow coloration with calcium chloride and with concentrated nitric acid. When a small crystal of ammonium molybdate is added to a solution of the hydrochloride in concentrated sulphuric acid a green zone, which subsequently turns blue, is formed round the crystal; the colour disappears on dilution

with water and reappears on heating. A green coloration is produced when a dichromate is used instead of ammonium molybdate.
CHEMICAL ABSTRACTS.

The Arsenotungstic Reagent in the Method of Bertrand and Javillier for the Estimation of Nicotine. LUIS GUGLIALMELLI and ULAUS HORDH (*Anal. Soc Quim. Argentina*, 1919, **7**, 121—123).—The preparation of silicotungstic acid for the estimation of nicotine by the method of Bertrand and Javellier (A., 1909, ii, 450) presents difficulties. The authors recommend the use of arsenotungstic acid (Guglialmelli, A., 1916, ii, 584, 587) as a precipitant. The procedure is otherwise unaltered. W. S. M.

Ehrlich's Reaction with *p*-Dimethylaminobenzaldehyde and Urorosein. E. SALKOWSKI (*Biochem. Zeitsch.*, 1919, **97**, 123—129).—The reaction of *p*-dimethylaminobenzaldehyde with indole, indoleacetic, indolepropionic and indoleaminopropionic acids is described and discussed. Herter's theory concerning the origin of urorosein in urine is also discussed. S. S. Z.

Estimation of Tyrosine by means of Millon's Reaction. MORIZ WEISS (*Biochem. Zeitsch.*, 1919, **97**, 170—176).—A 1/50,000 solution of tyrosine to which Millon's reagent is added is used as a standard. The solution to be examined is then diluted until it gives with Millon's reagent a coloration equal to that of the standard. The method can be employed for the estimation of tyrosine in the products of hydrolysis of proteins. S. S. Z.

New Method of Estimating Albumin in Urine. DOMENICO GANASSINI and PIETRO FABBRI (*Boll. Chim. Farm.*, 1919, **58**, 313—319).—A method of estimating albumin in urine is based on the fact that the sulphur of the cystinic group in the protein molecule is readily detached by the action of hot alkali hydroxide, and in presence of lead plumbite yields lead sulphide. On then titrating the liquid with iodine solution, the metaproteins are first oxidised and iodised, and the lead sulphide is then converted into lead sulphate. In applying the method, from 20 to 100 c.c. of urine (according to the amount of albumin indicated by a preliminary test) are mixed with 5% of sodium dihydrogen phosphate (to prevent precipitation of phosphates of alkaline earth metals), and the liquid heated and stirred for a few seconds until the albumin has coagulated. The precipitate is separated, washed, and dissolved in 10 to 30 c.c. of 10% potassium hydroxide solution, from 3·3 to 10 c.c. of 5% normal lead acetate solution added, and the beaker immersed for five minutes in boiling water. The liquid is then cooled to 21° and titrated with $N/10$-iodine solution, which is added at the rate of two drops per second, with continual stirring, until the liquid becomes colourless. The number of c.c. of iodine multiplied by 0·0330 gives the quantity of albumin in the amount of urine taken. Standard potassium ferricyanide solution may be used instead of iodine solution for the titration, but the end-point of the reaction is not so sharp. C. A. M.

Medical Analysis of Urine by the Combined Use of Tungstic Acid and Other Reagents. HUGH CAMPBELL ROSS (Brit. Pat., 134710).—When to 2 c.c. of urine 0·2 c.c. of a reagent composed of a 12% aqueous solution of colloidal tungstic acid to which 10% of acetic or tartaric acid to neutralise any possible alkalinity of the urine, and 2·5% of sodium potassium tartrate have been added, the presence of albumin is indicated by the formation of a precipitate which does not dissolve on warming. If the acid is impure, an excess of urates also causes a precipitate, but it redissolves on boiling the solution. In the latter case, a diabetic condition is indicated, and the presence of reducing sugars may be tested for by adding copper sulphate and an alkali hydroxide, or preferably, for the sake of convenience, a tablet containing 0·02 gram of copper sulphate and 0·01 gram each of sodium carbonate and calcium hydroxide. G. F. M.

Volumetric Analysis of Ion-protein Compounds. JACQUES LOEB (*Proc. Soc. Exp. Biol. Med.*, 1918, **16**, 39).—Gelatin at $p_H > 4·7$ combines only with cations and at $p_H < 4·7$ only with anions, whilst at the isoelectric point ($p_H = 4·7$) it combines with neither anion nor cation. Curves representing the influence of univalent anions or cations on the swelling, osmotic pressure, and viscosity of gelatin are always approximately parallel with the curves representing the amount of anion or cation found in chemical combination with the gelatin. CHEMICAL ABSTRACTS.

Estimation of Pepsin. JOHN H. NORTHROP (*J. Gen. Physiol.* 1919, **2**, 113—120).—See this vol., i, 193.

Influence of Acetic Acid on the Benzidine Reaction EMMO SCHLESINGER and JULIUS GATTNER (*Berl. Klin. Woch.*, 1919 **56**, 706—707; from *Chem. Zentr.*, 1919, iv, 526).—The discordant views of different authors on the value of the benzidine reaction in the detection of blood are due to the previously unnoticed fact that the sensitiveness of the reaction is a function of the concentration of the benzidine in the acetic acid. The authors find that a blue substance is the actual product of the benzidine reaction; this precipitated if the proportion of acetic acid to benzidine is low and is thus removed from further action and remains stable for long period. In the presence of an excess of acetic acid, however it dissolves, with the formation of a very unstable, green solution Diagnostic conclusions cannot therefore be immediately based on the occurrence of one or other coloration, since the quantity acetic acid used is a decisive factor. The blue colour invariably becomes green on addition of acetic acid. H. W.

Reduced Eosin as a Reagent. LUCIANO P. J. PALET and AMANCIO FERNANDEZ (*Anal. Soc. Quim. Argentina*, 1918, 119—120).—Traces of blood in dilute solution may be detected means of the fluorescence produced with an alkaline solution of the leuco-derivative of eosin. The substitution of fluorescein for eosin recommended. W. S. M

General and Physical Chemistry.

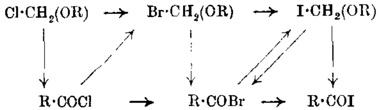
The Optics of Disperse Systems. III. I. LIFSCHITZ and GEORG BECK (*Kolloid Zeitsch.*, 1920, **26**, 10—15. Compare A., 1918, ii, 181, 253).—The authors have measured the refractive index of solutions of triethylamine, gelatin, and phenol in water and of silicic acid, stannic acid, arsenic sulphide, antimony sulphide, and vanadium pentoxide sols in water by the method previously described (*loc. cit.*). The measurements were made at a series of temperatures with the object of ascertaining the effect of change in the dispersity on the refractive index. It is shown that the degree of dispersion is practically without effect on the refractive index. In the cases of phenol and triethylamine, where on lowering the temperature beyond the critical solution temperature a separation of the two liquids occurs, there is only a very small change of refractive index shown. In the case of gelatin the value of the specific refraction varies very much with the temperature, whether calculated by the Gladstone and Dale formula or by the Lorenz and Lorentz formula. In all other cases the value is approximately constant when either formula is used, but the values given by the Gladstone and Dale formula are more nearly constant than the others. J. F. S.

The Spectrochemical Behaviour of Halogen Ethers, $RO\cdot[CH_2]_n\cdot X$, Halogen Hydrins, $HO\cdot[CH_2]_n\cdot X$, and Acid Bromides, $R\cdot COBr$. A. KARVONEN (*Acad. Sci. Fennicae*, 1914, *A*, **5**, 1—139; from *Chem. Zentr.*, 1919, iii, 807—808).—In continuation of previous work (A., 1913, i, 2) a series of halogen ethers and halogen hydrins has been refractometrically investigated. New values for the atomic refraction of chlorine, bromine, iodine, and oxygen have been deduced from observations on normal primary alkyl monohaloids and the mono-ethers of normal primary alcohols. The data obtained for chlorine and iodine agree excellently with Eisenlohr's figures; on the other hand, the new values for bromine and ethereal oxygen differ considerably from the older results. The following figures are quoted:

	H_α.	D.	H_β.	H_γ.	$H_\beta - H_\alpha$.	$H_\gamma - H_\alpha$.
$Br-CH_2-$	8·688	8·748	8·888	9·010	0·199	0·318
$O<\{CH_2-, CH_2-\}$	1·721	1·728	1·738	1·755	0·017	0·033

The α-halogen ethers, particularly the iodo- and bromo-derivatives, show optical exaltations in the order $Cl\cdot CH_2(OR) < Br\cdot CH_2(OR) < I\cdot CH_2(OR)$, whilst the behaviour of the β- and γ-halogen ethers and of the β- and γ-halogenhydrins is normal.

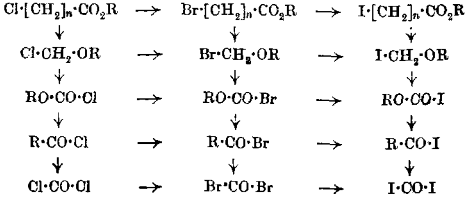
The acid bromides, like the corresponding chlorides, exhibit optica exaltation, the order being R·COCl<R·COBr<R·COI. The atomi refraction of bromine in acid bromides is H_α 9·514, D 9·595 H_β 9·805, H_γ 9·987, $H_\beta - H_\alpha$ 0·292, $H_\gamma - H_\alpha$ 0·467. Among the con pounds $X{\cdot}CH_2(OR)$ and R·CO·X the optical exaltations increas in the direction of the arrows:



When substituents, such as the halogens alone or with oxygen c alkyl groups, accumulate around a carbon, nitrogen, or phosphoru atom, the optical exaltations fairly generally increase and th depression diminishes. The reverse behaviour is particularly notic able when the atom adjacent to the central atom is attached to number of substituents or is multiply linked. The accumulation c ethereal groups appears generally to have a depressing influence.

H. W.

Influence of Position and Accumulation of Substituent on Spectrochemical Behaviour. II. The Spectrochemistr of Halogen and Oxygen Compounds. A. Karvonen (*Acac Sci. Fennicae*, 1916, *A*, **10**, No. 4, 1—22; from *Chem. Zentr.*, 1919 iii, 808. Compare preceding abstract).—The exaltation caused b the accumulation of chlorine and oxygen atoms has been confirme by observations on a series of chlorinated aliphatic esters. I general, the optical exaltation diminishes when the halogen aton in the chain are further removed from one another or from th oxygen atom. The esters of aliphatic acids containing a chlorir atom attached to the terminal carbon atom appear to exhibit slight optical depression. In the annexed combinations, the optica exaltations increase in the direction of the arrows:



H. W.

Influence of Position and Accumulation of Substituents on Spectrochemical Behaviour. III. Spectrochemical Behaviour of the Esters of Normal Acids of the Oxalic Series. A. KARVONEN (*Acad. Sci. Fennicae*, 1916, *A*, **10**, No. 5, 1—20; from *Chem. Zentr.*, 1919, iii, 811. Compare preceding abstracts).—Optical investigation of the methyl and ethyl esters of the oxalic series shows that the exaltation diminishes uniformly as far as the succinic esters with increasing separation of the carboxyalkyl groups. The oxalic esters show slight exaltation, malonic esters behave normally, and the succeeding esters exhibit a slight depression with a tendency to increase in refraction towards the higher members. Esters of suberic and sebacic acids behave similarly to other esters of the oxalic series. H. W.

Influence of Position and Accumulation of Substituents on Spectrochemical Behaviour. IV. Spectrochemical Behaviour of Ether-Esters, $RO\cdot[CH_2]_n\cdot CO_2R$. A. KARVONEN (*Acad. Sci. Fennicae*, 1916, *A*, **10**, No. 6, 1—14; from *Chem. Zentr.*, 1919, iii, 811. Compare preceding abstracts).—The following substances have been investigated: ethyl and methyl carbonates, methyl methoxyacetate, ethyl ethoxyacetate, propyl propoxyacetate, methyl *β*-methoxypropionate, ethyl *β*-ethoxypropionate, propyl *β*-propoxypropionate, methyl *α*-methoxypropionate, and ethyl *α*-ethoxypropionate. In the case of the lower fatty esters, the optical values diminish when a hydrogen atom of the acid radicle is replaced by an alkyloxy-group. The optical depressions diminish as the ethereal oxygen atom and the carlbonyl group become more distantly separated in the alkyloxy-aliphatic esters.
H. W.

Secondary Spectrum of Hydrogen. T. R. MERTON (*Proc. Roy. Soc.*, 1920, [*A*], **96**, 382—388).—The spectrum of hydrogen at 1 mm. pressure, and of hydrogen in helium at 40 mm. pressure have been photographed, using a concave grating 120 cm. radius of curvature and ruled 8000 lines per cm. It is shown that the lines of the secondary hydrogen spectrum in the red and yellow regions are greatly enhanced in the presence of helium, and that other new lines appear. In the more refrangible parts of the spectrum there is little difference in the intensity of the lines in the two cases. A second class of lines is not affected at all by the presence of helium, whilst a third class diminishes in intensity and in some cases disappears entirely. It is suggested that the change in intensity under the experimental conditions may serve as a method of investigation of the secondary hydrogen spectrum. Photographs of both spectra are given over the range λ 4300—λ 6500. A tabulated list of the lines which are not affected and of those which are enhanced in the presence of helium together with the intensities under the two sets of conditions is appended to the paper. The lines λ 5831·26 and 5703·86 are enhanced from intensity 2 to 7, 5819·60 from 2 to 8, and λ 5812·84 from 6 to 10. J. F. S.

Series of Multiple Lines in the Argon Spectrum. KNUD AAGE NISSEN (*Physikal. Zeitsch.*, 1920, **21**, 25—28).—A theoretical paper in which the lines of the argon spectrum are arranged into series. J. F. S.

Spectra of Isotopes. T. R. MERTON (*Proc. Roy. Soc.*, 1920, [*A*], **96**, 388—395).—The spectra of ordinary lead, lead from pitchblende and lead from thorite, ordinary thallium and thallium from pitchblende have been examined. An arc was produced between a tungsten button and the metal under investigation, in a bell jar at a pressure of 1 mm. The respective interference fringes produced by means of a Fabry and Perot étalon were photographed and measured by a micrometer. It is found that the line λ 4058 in the case of pitchblende lead has a slightly greater wave-length than in the case of ordinary lead, whilst for lead from thorite, it is somewhat shorter. The measurements in the case of thallium are not conclusive because pure thallium was not isolated from pitchblende. J. F. S.

A Relation between the Heads of Banded Spectra belonging to Different Elements of the same Group. TOKIHARU OKAYA (*Proc. Phys. Math. Soc. Japan*, 1919, [3], **1**, 111—121).—It is shown that for the three elements gold, copper, and silver the wave-lengths of the heads of bands emitted by their molecules satisfy fairly well the linear relation $\lambda=\alpha+\beta n$, where α and β are constants and n is the series of natural numbers. From this it is concluded that between the heads of the band spectra emitted by the different molecules in similar conditions there exists a simple relation when the bands diverge toward the red side. Thus, the wave-length λ of the head of some band of one element with reference to the corresponding one λ' of another element is given by the relation $\lambda=(\alpha+\beta n)(m/m^1)^{\frac{1}{2}}(p/q)^{\frac{1}{2}}$, p and q being certain integers, m and m^1 the atomic weights of the elements concerned, and $\lambda'=(\alpha+\beta n)$. CHEMICAL ABSTRACTS.

Spectra of Tin, Lead, Antimony, and Bismuth in a Magnetic Field. P. A. VAN DER HARST (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 300—312).—Using the light from a condensed spark between poles of tin, lead, antimony, and bismuth respectively, the author has examined the effect of a magnetic field of about 30,000 gauss on a number of lines of these metals. The Zeeman effect is measured for 35 lines of tin, 23 of lead, 27 of antimony, and 16 of bismuth. The measurements show deviations from those previously published by Purvis (A., 1907, ii, 919), due to uncertainty in the strength of the field used by Purvis. The resolutions of the lines are fairly regularly distributed between values which are 1—1·5 times the normal resolution. Incidentally, it is shown that the antimony lines λλ 4370, 4295, 4287, 4091, 4078, 4038, 4024, 4006, 4004, 3979, 3721, 3467, and 3460 measured by Schippers (A., 1912, ii, 877), and published in Kayser's "Handbuch der Spectroscopie," do not exist. The lines are respectively

λλ 2913, 2863, 2858, 2727, 2719, 2692, 2683, 2671, 2670, 2653, 2480, 2311, and 2306. The error has arisen by Schippers mistaking lines of the third order for lines of the second order. J. F. S.

Colour of Metallic Salts. YUSI SHIBATA (*J. Tokyo Chem. Soc.*, 1919, **40**, 463—482).—From the spectral analysis of compounds of cobalt, nickel, and chromium the author deduces that *the region of colour formation in these salts lies between the non-metallic atomic group and the metallic group which form a nucleus for the complex ions or double salts. In no case is colour developed* by metallic salts without the formation of complex ions. Colourless complex inorganic salts which show *strong absorption in the* ultra-violet are composed of constituents which are absolutely transparent in this region. A theory is developed which leads to the conclusion that the wave-length of the light absorbed is longer the smaller is the atomic volume of the metal forming the centre of the complex. The conclusion is supported by experimental evidence in the case of correspondingly constituted complex salts of zinc, platinum, copper, tin, silver, cadmium, and mercury.

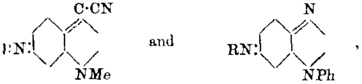
The application of the theory to chromophores in organic compounds is discussed. CHEMICAL ABSTRACTS.

Relation between the Visible Absorption Spectra of certain Metals in their $M^{iv}X_4'$ and $(M_2)^{vi}X_6'$ Derivatives. MATHEUS D'ANDRADE ALBUQUERQUE (*Revista Chim. pura applic.*, 1916, **1**, Reprint 14 pp.).—In order to verify the law of the conservation of even or odd valencies in derivatives of the same element, evidence was sought for the existence of molecules of the type M_2X_6' in salts derived from sesquioxides. A number of coloured salts with colourless anions were investigated in non-dissociating solvents, or compounds containing complexes, such as K_2MX_6 and K_3MX_6. Two methods were available: (1) combination of two different salts of the type M_2X_6 so as to obtain a mixed salt $MM'X_6$; if the properties of the latter were different from those of M_2X_6 and $(M')_2X_6$, the difference must be attributed to linking between M and M'; (2) spectrographic evidence for some union between M and M'. The observation of the absorption spectra proved that the normal salts derived from sesquioxides always presented absorption bands, most of which were in the region where salts of the type MX_4 of the same element show no absorption. When an element combines with another in different proportions, the colour of the compounds shifts towards the red end of the spectrum as the valency increases; and as the colour of sesquioxide salts is often abnormal, this must be attributed to a radicle which can only be M_2. In the iridichlorides of silver and thallium the author assumes the presence of a complex radicle containing iridium because, unlike other reddish-brown iridichlorides, the salts are blue and bluish-green respectively, that is, approximating towards the colour of $IrCl_3$ or Ir_2Cl_6. It is observed that didymium gives a characteristic absorption spectrum differing from those of praseodymium and neodym-

ium, which points to the existence of an atomic complex. In the majority of cases the colour of salts of the type M_2X_6 is complementary to that of the salts MX_4 of the same element, a property which will be discussed in a future paper. W. R. S.

Absorption Bands in the Ultra-violet and Magnetic Birefraction. GUSTAVE MASSOL and A. FAUCON (*Bull. Soc. chim.*, 1919, [iv], **25**, 585—588).—It is shown that the substances or groups which give absorption bands in the ultra-violet also exhibit magnetic birefraction as found by Cotton and Mouton (compare A., 1910, ii, 368). W. G.

Quinone-imide Dyes. XII. Absorption Spectra of some Cyanoacridine and Cyanopyronine Dyes. F. KEHRMANN and M. SANDOZ (*Ber.*, 1920, **53**, [*B*], 63—66).—In an earlier paper (A., 1918, i, 313) it was shown that the substitution of the group ⁝C·C⁝N for the tervalent nitrogen atom in safranines and azoxines has practically no effect on the colour. The absorption spectra for three sets of comparable dyes have now been determined, revealing the same feature. In fact, the groups



especially may be regarded as optically equivalent. J. C. W.

Determination of the Constitution of Coloured Substances from their Absorption Spectra. II. F. KEHRMANN and MAURICE SANDOZ (*Helv. Chim. Acta*, 1920, **3**, 104—114. Compare A., 1918, ii, 418).—The absorption spectra of the mono- and di-amino- and of the dianilino-phenazines have been examined.

Alcoholic solutions of phenazine and aminophenazine are almost colourless and orange respectively, whilst similar solutions of *s.*- and 2:3-diaminophenazines are pale yellow and very light yellow; this is in accordance with the authors' theory that the introduction of an amino-group in the para-position to the nitrogen of quinone-imines or in the same position with respect to the carbon atom of triphenylmethane has a hypsochromic or bathochromic influence which depends on the basicity of the group into which it enters. The introduction of the first amino-group into phenazine considerably increases the basicity, but this is not the case with the second group. Phenylated derivatives of phenazine are slightly more red than the corresponding non-phenylated compounds, but are chiefly noticeable for the augmentation of the intensity of colour effected by introduction of the phenyl group. In general, the absorption curves of the bases do not present any striking anomalies, and the authors therefore attribute to them the orthoquinonoid structure of phenazine itself.

Mono- and di-aminophenazines have very similar absorption spectra when dissolved in fuming sulphuric acid, which closely resemble that of the di-acid salt of phenazine; they appear, therefore, to have the orthoquinonoid structure, the imino-groups having lost their auxochromic effect by conversion into amino-salts. When, however, the solutions are gradually diluted with concentrated sulphuric acid, the blood-red colour suddenly changes to green, the shade differing somewhat with the individual compound. The gradual dilution of the acid appears to cause hydrolysis of the poly-acid salts and to liberate one by one the auxochrome groups, the activity of which has been paralysed by salt-formation. Thus the green shade of the tri-acid salt of diaminophenazine gradually gives place to the violet tint of the di-acid salt and to the cherry coloration of the mono-acid salt. Since the successive transformations take place in a continuous manner without appearance of any striking anomalies, the authors ascribe the paraquinonoid constitution to the di-acid and mono-acid salts, as well as to the green tri-acid compounds.

The ultra-violet spectra of the bases and of the mono-acid salts have been examined. With the former, an absorption band is invariably observed, which becomes progressively displaced towards the visible violet as the chromogen becomes more highly substituted; it is situated at $\lambda=250\ \mu\mu$ for phenazine, at $\lambda=265\ \mu\mu$ for the mono- and di-aminophenazines, and at $\lambda=285\ \mu\mu$ for dianilinophenazines. The position of the anilino-groups which has such a marked influence on the position of the bands in the visible spectrum appears to have no effect on the location of the band in the ultra-violet. The mono-acid salt of aminophenazine gives two bands in the ultra-violet, that of 1 : 2-diaminophenazine has one band in the visible violet ($\lambda=457\ \mu\mu$), whilst the second is but slightly shifted; that of *s*-diaminophenazine shows only one band in the ultra-violet, the second having completely disappeared. The mono-acid salts of the anilinophenazines likewise only show one band in the ultra-violet ($\lambda=285\ \mu\mu$). It appears, therefore, that isomeric substances with equal molecular weights give superposable spectra in the ultra-violet. H. W.

Photochemical Actions produced in Crystals by means of Polarised Light. M. Padoa (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 372—377).—The author has studied the action of polarised light on crystals of cinnamic acid, *o*-nitrobenzaldehyde, and cinnamylidenemalonic acid (compare Weigert, A., 1918, ii, 344), all of which compounds undergo pronounced photochemical transformations.

After exposure to the action of light, crystals of cinnamic acid become dulled, the dimeric α-truxillic acid being formed (compare Stobbe, A., 1919, i, 329). Since this action is manifest only after prolonged exposure, it may be assumed that solid solutions between the monomeric and dimeric forms are first formed; that such solutions are supersaturated is confirmed by the normal cryoscopic

behaviour of α-truxillic acid in cinnamic acid solution, and melting-point measurements indicate the concentration limit of the supersaturated solutions to be 3% of the truxillic acid. No appreciably different results were obtained on exposing crystals of cinnamic acid to the action of polarised light, in the one case with the plane of polarisation parallel, and in the other normal, to one pair of parallel edges of the crystal.

When two prismatic crystals of *o*-nitrobenzaldehyde (compare Lobry de Bruyn and Jungius, A., 1903, ii, 531; Bruni and Callegari, A., 1904, ii, 545) are crossed normally and exposed in a polarising microscope to the influence of polarised light with the plane of polarisation at 45° to the axes of the two crystals, one of the latter undergoes change more rapidly than the other.

Results similar to, but more pronounced than, those obtained with *o*-nitrobenzaldehyde are observed in the case of cinnamylidene-malonic acid. After an exposure to the action of polarised light varying, according to the magnitude of the crystals, from one and three-quarters to three hours, part of the crystal, with its axis perpendicular to the plane of polarisation, is violently detached and often projected to a distance; in some cases, however, only transverse segmentations appear in the crystals, such occurring earlier and in greater number in the crystal mentioned. Subsequently, crystalline nodules of the dimeride make their appearance. Here too it may be assumed that solid solutions of the dimeride in the monomeride are first formed, these solutions being so unstable as to produce a condition of tension in the crystals, and consequent explosion. The partial transformation of the monomeride into the dimeride may be followed by means of the melting point, which shows marked lowering even before any change in the crystal is apparent.

Weigert's conclusions are criticised, and arguments are advanced in support of the view that phototropy is to be classed among the real photochemical phenomena. T. H. P.

Behaviour of Fehling's Solution in Light. IVAN BOLIN and GUNNAR LINDER (*Zeitsch. physikal. Chem.*, 1919, **93**, 721—736).—The action of light from a carbon arc on Fehling's solution in glass and quartz vessels has been studied at 15° and 25°. The amount of cuprous oxide precipitated was estimated by titration with potassium permanganate. The light reactions were compared with the reactions occurring in the dark. It is shown that in glass vessels the reaction has no temperature-coefficient, and that there is no evolution of gas. The velocity of reaction is proportional to the time during which the solution has been illuminated, and on removing the light the reaction ceases. In quartz vessels, the reaction has a temperature-coefficient 1·2, and after about three hours' illumination there is an evolution of gas. The velocity of the reaction increases with the time of illumination, and when the light is removed, the reaction continues for some time. The difference in the course of the reaction in glass and quartz vessels is explained

is follows. In quartz vessels, in addition to the photochemical reaction, an ordinary chemical reaction also takes place. This reaction is caused by substances produced in the photo-reaction. Both reactions produce cuprous oxide, the chemical reaction increasingly more as reducing substances are produced photochemically. Consequently, the total amount of cuprous oxide produced increases progressively with the time. On shutting off the light, the reaction continues until all the reducing substances have been used up. The reaction is more pronounced in quartz vessels, because these allow light of smaller wave-length than 350 $\mu\mu$ to enter the liquid, and it is due to these waves that the reducing substances are produced from the tartrate in the solution. J. F. S.

The Recoil of α-Particles from Light Atoms. L. B. Loeb (*Phil. Mag.*, 1919, [vi], **38**, 533—541).—An account is given of an attempt to verify the conclusion of Rutherford, namely, that in collisions between α-particles and light atoms, the number of atoms projected straight forward within an angle of 10° from that of the α-particle is ten to thirty times that calculated from Darwin's theory of point charges, by examining the number of α-particles recoiling after collision with light atoms. The conditions necessary to ensure success and overcome the numerous difficulties are worked out, but the results are provisional and indecisive for lack of sufficient time. They indicate that for aluminium the abnormalities found by Rutherford for nitrogen and hydrogen begin to show themselves, but the experimental difficulties were not overcome for lighter elements, such as carbon. The range of the α-particle deflected at 105° from aluminium was found to be below 3·6 cm., as is to be expected if the laws of energy and momentum apply to these close encounters. F. S.

Passage of Corpuscular Rays through Material and the Constitution of the Atom. I. R. Seeliger (*Jahrb. Radioaktiv. Elektronik*, 1919, **16**, 19—65).—A theoretical paper in which the author discusses the work of many investigators on the passage of α- and β-rays through material. The consideration is concerned with the individual processes and changes brought about by the passage of a corpuscular ray through an atom or a molecule. These changes are subdivided into changes in the moving particle: (i) direct conveyance of kinetic energy to the atom, and (ii) emission of electromagnetic radiation; and into changes in the atom: (i) direct gain in kinetic energy, (ii) emission of electromagnetic radiation, (iii) emission of secondary corpuscular radiation, and (iv) chemical changes. J. F. S.

Connexion between Collision Ionisation and the Energy of Ionisation of Neutral Molecules. J. Franck, P. Knipping, and Thea Krüger (*Ber. Deut. physikal. Ges.*, 1919, **21**, 728—732).—The ionisation steps of hydrogen have been investigated. It is shown that definite ionisation occurs at 11·5±0·7 volts, 17·1±0·25

volts, and 30·4±0·5 volts. The first step corresponds with th formation of $H_2^{\cdot}$, and the measurements show that an ion wit considerably larger diameter is formed at 11·5 volts than at 17 o 30 volts. At 13·6±0·7 volts there is an emission of ultra-viole light, the potential 17·1±0·25 volts corresponds with the ionisatio of the atom into a normal, and a positive ion and an electron, an the potential 30·4±0·5 volts corresponds with ionisation of the ator into two positive ions and two electrons. These results go to shov that the Bohr atom model of hydrogen is not strictly in keepin with the facts. J. F. S.

Apparatus for the Separation of Radium Emanatio and its Estimation Electroscopically. J. E. UNDERWOOD an HERMAN SCHLUNDT (*Trans. Amer. Electrochem. Soc.*, 1918, **34** 203—209).—An apparatus is described by means of which radiun in various ores and concentrates may be estimated. The materia is either boiled with concentrated sulphuric acid or fused with mixture of alkali carbonates or with sodium hydrogen sulphate i one part of the apparatus, and the emanation stored in a mercur burette in another part of the apparatus. The emanation is kep for ten minutes in the burette to allow the thorium emanation t decay, and is then passed into the electroscope, where it is measured in the usual way. Using this method, Brazilian monazite is shown to contain 0·794—0·812 × 10^{-7} gram radium per gram; Indian monazite, 0·1017—0·1025 × 10^{-7} gram radium per gram. J. F. S.

Comparison of the Ionisation Currents due to Equal Quantities of Radium Emanation in Different Types o Electroscopes. T. H. LEAMING, HERMAN SCHLUNDT, and JULIUS E UNDERWOOD (*Trans. Amer. Electrochem. Soc.*, 1916, **30**, 365—378) —The authors have compared the ionisation currents obtained with several types of electroscopes (Lind, Wulf quartz fibre, Fontacto-meter, Duane and Laborde, and Randall), and find that, with the exception of the Randall rectangular electroscope, the measured currents have lower values than the values calculated by the formula of Duane and Laborde, $I=K(I-C.S/V)$. In some cases, the values were 18—22% too low. The experiments show that the reduction factor, C, of Duane and Laborde's formula has specific values for ionisation chambers of definite dimensions. J. F. S.

Absorption of Radium Gamma Rays. K. W. F. KOHLRAUSCH (*Sitzungsber. K. Akad. Wiss. Wien*, 1917, **126**, *IIa*, 683—704).—The results of the investigation are given in the following table, where K_1, K_2, and K_3 are the three components of the complex γ-rays from radium:

Absorption Coefficients μ_1, μ_2, *and* μ_3.

Absorber.	K_1.	K_2.	K_3.
Lead	0·545	1·4	4·6
Zinc	0·327	0·57	1·44
Iron	0·356	0·63	3·00
Aluminium	0·127	0·23	0·57

The ratio of the energies measured by ionisation currents is, for *these three components*, $K_3 : K_2 : K_1 = 1 : 6 : 8$. The absorption measurements show that the influence of secondary radiation is *extremely important.* CHEMICAL ABSTRACTS.

The Hard Secondary Gamma Rays from Radium. K. W. F. KOHLRAUSCH (*Sitzungsber. K. Akad. Wiss. Wien*, 1917, **126**, IIa, 705—720).—In a previous paper (compare preceding abstract) the author made a careful series of measurements of the absorption of the γ-rays of radium in various snbstances. In these experiments, the importance of secondary radiation was indicated. The present paper deals with this secondary radiation, which is shown to have a high penetrating power. When the γ-rays pass through matter, a very hard type of secondary radiation ($\mu_{Pb} = 0.545$ cm.$^{-1}$) is produced. The author compares the observed total energy of the secondary radiation with the calculated values for varying thickness of screen. The observations are in good agreement with theory. CHEMICAL ABSTRACTS.

Absorption of Gamma Rays from Radium. K. W. F. KOHLRAUSCH (*Sitzungsber. K. Akad. Wiss. Wien*, 1917, **126**, IIa, 887—913).—The results are given of an extensive series of measure*ments of the absorption coefficients of radium γ-rays in different* substances. CHEMICAL ABSTRACTS.

The Chemical Character of Protoactinium [Ekatantalum]. I. Separation of Protoactinium from Pitchblende. OTTO HAHN and LISE MEITNER (*Ber.*, 1919, [*B*], **52**, 1812—1828). —The raw material for the preparation of protoactinium is the insoluble residue, consisting principally of silica, from pitchblende after treatment of the mineral with nitric acid. By repeated extraction with nitric acid, all the radioactive substances, including radium, can be dissolved, and the residue left with a very feeble α-activity, due chiefly to protoactinium. It is recommended to add from ½% to 1% of tantalum oxide to the pitchblende residue and to heat it with a little concentrated sulphuric acid and excess of 40% hydrofluoric acid in a platinum capsule covered with a platinum dish containing cold water to serve as a condenser, then to dilute and filter through a paraffined funnel, evaporate the filtrate, and ignite the residue gently, which renders the tantalum oxide containing the protoactinium insoluble in acids. An addition of a few milligrams of thorium and of lead nitrates to the hydrofluoric acid serves to keep traces of ionium, uranium-*X*, and radio-lead from passing through the filter with the tantalum. The ignited tantalum oxide is boiled with aqua regia to remove iron, zirconium, etc., leaving the tantalum undissolved.

The Rutherford-Boltwood ratio of 8% for the actinium branch series would, neglecting correction for difference of range, lead to an α-activity of proto-actinium 4% of that of the uranium in the mineral from which it is extracted. This is found to be much too high. The protoactinium was separated from known amounts of

pitchblende by three different methods, detailed below, and the α-activity of the preparation extracted per gram of mineral was found to be the same, within 10%, in six experiments, from which, after applying a correction for the range, it is calculated that only 3% of the atoms of uranium disintegrating pass through the proto-actinium, actinium series. The three methods consist of: (1) fusion of the pitchblende with sodium hydrogen sulphate, followed by treatment of the insoluble residue with hydrofluoric acid, as already detailed; (2) treatment of the very finely divided mineral with hydrofluoric acid and sulphuric acid, in which the main part of the protoactinium passes into solution directly; (3) treatment of the mineral very similarly to that described already for the residue. Full details of the chemical operations and charts are given showing, in each case, the distribution of the radio-elements in the successive stages of treatment. Tantalum oxide was always added to the mineral, and elaborate care taken, more of this material being added and separated from each of the separate parts to remove proto-actinium, to ensure that all was separated. Finally, as a test, a known amount of previously prepared protoactinium preparation was added to pitchblende, and the result showed that no loss, exceeding 5%, occurred in the course of the chemical treatment.

The low percentage of the actinium series operates against sufficient protoactinium being present in uranium minerals for isolation like radium. Its period of average life can only be fixed within the limits of 1200 and 180,000 years at present, which correspond with weights in the mineral of 1·5% and 22·5% of the weight of contained radium. So far, efforts to concentrate it from tantalum have failed. It is suggested that an examination of the amount of protoactinium in old uranium preparations might throw further light on the period, and uranium preparations of known age of uranium, not less than 100 to 200 grams, are appealed for. The 3% ratio agrees with the ratio found for the relative activities of uranium-X_1 and uranium-Y. It is pointed out that protoactinium with atomic weight about 230 and place in the periodic table beyond thorium, of atomic weight 232, furnishes probably another example similar to that of tellurium and iodine. F. S.

The Origin of Actinium. OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1919, **20**, 529—533. Compare preceding abstract).—The paper contains some further details of the methods employed for determining the relative α-activity of the preparations measured. F. S.

Determination of the Half-life Periods of Thorium and Actinium Emanations. R. SCHMID (*Sitzungsber. K. Akad. Wiss. Wien*, 1917, **126**, IIa, 1065—1079).—The author describes a method which is the same in principle as that used by Leslie and Perkins. Measurements were also made by Rutherford's method, in which the ionisation current is measured at different points along a tube

through which the emanation is flowing at a known rate. A third method employed is due to Mache. The mean results of the investigation are as follows: half-life period for thorium emanation $54 \cdot 5 \pm 0 \cdot 03$ secs.; for actinium emanation $3 \cdot 92 \pm 0 \cdot 015$ secs.

CHEMICAL ABSTRACTS.

The Age of Thorium Minerals. R. W. LAWSON (*Sitzungsber. K. Akad. Wiss. Wien*, 1917, **126**, IIa, 721—739).—The paper deals with the end-product of the thorium series in the light of the atomic weight results of Hönigschmid and others. It is shown that the age, determined from the Th/U and Pb/U ratios, may be between 8 and 300 million years. The minerals employed came from Devon, Brevig, and Norway. The possible origin of the large discrepancy in age is discussed. Thorium minerals from Ceylon give a range from 138 to 506 million years. CHEMICAL ABSTRACTS.

Electrolytic Dissociation Theory. GEORGE SENTER (*Trans. Faraday Soc.*, 1919, **15**, 3—9).—An introductory paper to a discussion of *The Present Position of the Theory of Ionisation* (see following abstracts), in which the author summarises certain investigations on electrolytes in solution, namely, hydration, deviation of strong electrolytes from the law of mass action, and the chemical activity of ions and non-ionised molecules. It may be regarded as established that ions and undissociated molecules may simultaneously undergo chemical change, and that in the catalytic activity of strong acids the non-ionised molecule plays a part as well as the hydrogen ion. J. R. P.

Electrolytic Dissociation. SVANTE ARRHENIUS (*Trans. Faraday Soc.*, 1919, **15**, 10—17).—The author summarises the present evidence in favour of the dissociation theory of solution under eleven headings: (1) Evidence from analytical chemistry. (2) Additive properties. (3) The diffusion of electrolytes. (4) The electric conductivity of solutions. (5) Colours of solutions. (6) Ostwald's law. (7) Non-aqueous solutions. (8) Ostwald's law for salt solutions in water. (9) The freezing point of aqueous solutions. (10) Deviations in concentrated solutions. (11) Velocity of reaction.

J. R. P.

Present Position of the Ionisation Theory: Reactions of both the Ions and Molecules of Acids, Salts, and Bases. S. F. ACREE (*Trans. Faraday Soc.*, 1919, **15**, 18—26).—Mainly an historical account of attempts to elucidate the so-called "abnormal salt effect" of dissolved electrolytes. Results on the inversion of sucrose and other reaction velocities are explained by assuming that molecules, as well as ions, are active. The acid molecules are found to be two or three times more active than the hydrion in the case of hydrochloric, hydrobromic, and nitric acids, as measured by the hydrolysis of sucrose. A similar conclusion was reached for the hydrolytic activity of alkalis. The activity of molecules is also deduced from a study of the action of alkyl haloids in alcoholic

solution on phenoxides. Another cause of abnormal salt effect i solvation, studied by Lapworth. Several tables of values of th velocity constants of ions and molecules, deduced from the author' results and from re-interpretation of those of other workers, ar given. J. R. P.

The Bearing of Migration Data on Conduction in Solutions. The Electrochemistry of Sodium Iodide in Acetone JAMES W. MCBAIN and F. C. COLEMAN (*Trans. Faraday Soc.*, 1919 **15**, 27—46).—When the sum of the movements of both ions i equal to the total current, the solvent cannot be appreciably dis sociated. This is the case in aqueous solutions. Hypotheses to th contrary are therefore invalidated. The migration data for solu tions of sodium iodide in acetone, and of silver bromate in diethyl amine, show that, even in highly concentrated solutions, the solven does not conduct appreciably. The evidence of the migration dat shows that conductivity is only an approximate measure of th degree of dissociation, since the migration ratio almost invariabl increases with the concentration, a change ascribed to solvation The calculation of conductivities at infinite dilution from extra polation of dilution formulæ to infinite dilution, or from th assumption of the law of mass action at infinite dilution, ar regarded with disfavour. The molecular weight of sodium iodid in acetone, determined by the boiling-point method, is normal.

J. R. P.

The Determination of the Ionisation of an Aqueous Solution. W. R. BOUSFIELD (*Trans. Faraday Soc.*, 1919, **15** 47—73).—A summary of the methods used by the author in calcu lating the ionisation of an electrolyte in aqueous solutions. Ion isation is assumed to be the result of the interaction of associated water molecules with the molecules of the salt, whereby (H_2O) and H_2O molecules react with the salt to produce $(H_2O)_2$ molecule and hydrated ions. The application of the law of mass action then gives equations which give good results for a large class of strong electrolytes at high dilutions, and in the case of the alkali chlorides give good results in concentrated solutions. On account of vary ing hydration, it is assumed that the transport numbers require correction. This, however, cannot at present be carried out excep by the method of trial and error. Stress is laid on the part played by the solvent, which is assumed to exist in associated forms, the proportions of which vary with the concentration of the solution.

J. R. P.

Correction of the Transference Numbers of the Ions of an Electrolyte. W. R. BOUSFIELD (*Trans. Faraday Soc.*, 1919, **15**. 74—80).—On the assumption that the volumes of the ions in solu tion are unequal, the correction necessary in the ordinary method of calculating the relative ionic mobilities from the transport numbers is found. The corrections are inappreciable at concentra tions less than normal. J. R. P.

Some Aspects of the Electrolytic Dissociation Theory. NILRATAN DHAR (*Trans. Faraday Soc.*, 1919, **15**, 81—93).—By a discussion of recent work on electrolytes, including molecular-weight determinations, Kohlrausch's rule, freezing points, osmotic pressures, heats of neutralisation of acids and bases, and absorption spectra, the conclusion is drawn that the theory of non-ionisation proposed by Snethlage (A., 1915, ii, 615, 825) is not tenable.

J. R. P.

The Hydration of Ions. HENRY J. S. SAND (*Trans. Faraday Soc.*, 1919, **15**, 94—97).—In his calculations of the radii of ions, Bousfield adopts a radius for the water molecule which leads to a value for Avogadro's constant over twenty times that adopted in the same calculations. The values for the ionic radii deduced from Stokes's law do not agree with those derived from other calculations. It is believed that it is incorrect to apply the law of Stokes to molecular magnitudes.

J. R. P.

Some Recent Investigations on the Dilution Law. J. R. PARTINGTON (*Trans. Faraday Soc.*, 1919, **15**, 98—121).—In the case of weak electrolytes the law of mass action applies with greater accuracy than to any other case yet investigated. The viscosity correction has been applied in a very arbitrary manner by many investigators, and the author believes that in dilute solutions it is unnecessary. The equation deduced by Szyskowski (A., 1915, ii, 616) gives very accurate results for strong electrolytes, and renders unnecessary the arbitrary alterations made by Kraus and Bray (A., 1913, ii, 914) in the accurate experimental values of Kohlrausch and Maltby (A., 1900, ii, 61). It is shown that the theory proposed by Ghosh (A., 1918, ii, 348, 392, 423) is not in accordance with the experimental results of the latter observers, since it requires equal ionisations at equal dilutions for all electrolytes of the same type, whereas differences are found. It is concluded that the law of mass action applies to strong electrolytes at great dilution.

J. R. P.

Variation of Electrical Conductivity of Electrolytes with Increase of Concentration. ALFRED W. PORTER (*Trans. Faraday Soc.*, 1919, **15**, 122—125).—The empirical equation of Kohlrausch, $1-\alpha=\text{const.}\times c^{\frac{1}{3}}$, is shown by a graphical method to hold over a large range. The index n of Storch's equation, $\alpha/(1-\alpha)^n=KV^{1-n}$, is practically the same for potassium chloride as for sodium sulphate, in spite of the difference in valency. This equation has the form required by the law of mass action for a possible reaction, although the particular reaction which makes $n=\frac{2}{3}$ (van't Hoff) has not yet been identified. The assumption of electrical action between the ions would lead to diminution of the ionisation α with concentration at a greater rate than required by the law of mass action, whereas the opposite effect is actually found. If the law of mass action holds good at great dilution, it is necessary to explain the transition from this to the other laws which hold

at increased concentrations. A possible equation is $a^2(1+ba/V)/(1-a)[1+c(1-a)/V]=\text{const.}$, where b and c are additional constants. J. R. P.

The Resistance of an Electrolytic Cell. EDGAR NEWBERY (*Trans. Faraday Soc.*, 1919, **15**, 126—136).—That part of the irreversible resistance of an electrolytic cell which is concerned in the *transfer of the current from electrode to electrolyte* has been studied in a number of cells. Transfer resistance is greatest when gases are liberated at the electrodes, considerable when gaseous ions are utilised in carrying the current, although not liberated at the electrodes, and negligibly small when the current is carried by metallic cations and by anions which readily dissolve the anode. Conditions favourable for high transfer resistance are low current density, low temperature, polished surfaces, and high over-voltages. Those conditions which affect the nature of the surfaces affect also the transfer resistance. Transfer resistance is due to the mechanical resistance (pressure and frictional) which opposes the penetration of gaseous ions into the surface of the electrodes. Measurements of electrical conductivity are liable to serious error if transfer resistance is not perfectly eliminated, and there is reason to fear that this has not been done in determining some of the conductivity data at present available. J. R. P.

Effect of Interionic Forces in Electrolytes. S. R. MILNER (*Trans. Faraday Soc.*, 1919, **15**, 148—151).—Chemical forces, which cause the association of two ions into a molecule, diminish extremely rapidly with the distance, and become negligible at very small separations of the ions, whereas electrical forces between the ions fall off comparatively slowly. The ordinary derivation of the law of mass action for electrolytes assumes that interionic forces become negligible for finite separations of the ions. These forces, however, would cause a reduction of osmotic pressure and of molecular lowering of freezing point. The application of the inverse square law leads to general agreement with the observed freezing-point curves. The conductivity should be proportional to the osmotic pressure of the free ions, that is, those possessing sufficient kinetic energy to escape from their attracting neighbonrs. J. R. P.

Ionisation and the Mass Law. H. M. DAWSON (*Trans. Faraday Soc.*, 1919, **15**, 152—153).—The deviations from the law of mass action in the case of strong electrolytes are ascribed mainly to changes in the ionising power of the solvent by the highly polar solutes. J. R. P.

The Abnormality of Strong Electrolytes. JNANENDRA CHANDRA GHOSH (*Trans. Faraday Soc.*, 1919, **15**, 154—163).—The author does not agree with the criticisms of Partington (see above). The deviation from his theory shown by some electrolytes is ascribed to hydration of the ions. J. R. P.

Equilibrium between Bromine and Potassium Bromide Solutions at 0°. GRINNELL JONES and MINER LOUIS HARTMANN (*Trans. Amer. Electrochem. Soc.*, 1916, **30**, 295—326).—Measurements of the equilibrium between bromine and water and between bromine and potassium bromide solutions at 0°, and of the specific conductivity of the solutions have been made. Calculations by the method of successive approximations based on the results show that the following reactions occur: (i) bromine dissolves as Br_2; (ii) $Br_2 + H_2O \rightleftharpoons H^{\cdot} + Br' + HBrO$; (iii) $KBr + Br_2 \rightleftharpoons KBr_3$; (iv) $KBr + 2Br_2 \rightleftharpoons KBr_5$. A saturated solution of bromine in water at 0° has the composition $Br_2 = 0{\cdot}2539$ mol. per litre; $H^{\cdot}$, 0·001085; Br', 0·000126; Br_3', 0·000628; and Br_5, 0·000331. The hydrolysis constant, $K_{\prime\prime} = (H^{\cdot})(Br')(HBrO)/Br_2 = 5{\cdot}7 \times 10^{-10}$, the equilibrium constant, $K_3 = Br' \times Br_2/Br_3' = 0{\cdot}051$; and the equilibrium constant, $K_5 = Br' \times Br_2^2/Br_5' = 0{\cdot}0246$. The partition-coefficient of Br_2 between water and carbon tetrachloride after correcting for hydrolysis is $D = 21{\cdot}018 + 2{\cdot}831C$, where C is the concentration of Br_2 in the carbon tetrachloride. By means of these constants the concentration of each ion may be calculated in any solution containing known amounts of potassium bromide up to $0{\cdot}1N$ and bromine up to saturation. The conductivity of a series of solutions of potassium bromide from $0{\cdot}001N$ to $0{\cdot}1N$ has been determined at 0°. When extrapolated to infinity by Noyes' method, these results give 83·8 for Δ_∞, and if the ionic conductivity of $K^{\cdot}$ is 40·1, Br' has the value 43·7. From the data for the specific conductivity of solutions of potassium bromide containing bromine it follows that the ionic conductivity of Br_3' is 23·5 and of Br_5', 16·3. J. F. S.

Corrosion of Metals by Acids. OLIVER P. WATTS and NEWTON D. WHIPPLE (*Trans. Amer. Electrochem. Soc.*, 1917, **32**, 257—284).—The rate of corrosion and solution of iron, zinc, zinc amalgam, mercury, cadmium, tin, lead, copper, gold, silver, tin amalgam, and lead amalgam by means of hydrochloric acid, sulphuric acid, perchloric acid, phosphoric acid, and acetic acid, and also by solution of sodium hydroxide and a series of salts, has been determiued. The effect of a number of oxidising agents on the rate of solution has also been investigated. The following oxidising agents were used: hydrogen peroxide, sodium arsenate, ferric sulphate, ferric chloride, potassium dichromate, potassium chlorate, mercuric chloride, potassium permanganate, potassium nitrate, chromic anhydride, nitric acid, potassium bromide, sodium nitrite, and potassium iodide. The authors confirm the view previously put forward (*ibid.*, 1912, **21**, 340) that the protective effect of arsenic on the corrosion of iron by sulphuric acid is due to polarisation by hydrogen. This view is confirmed by the facts that the corrosion of iron by acids when the metal was protected by arsenic was greatly accelerated by oxidising agents and arsenic does not protect iron from attack by corrosive agents which do not evolve hydrogen by their action. Amalgamation protects zinc from corrosion by acids because the discharge potential of hydrogen on mercury exceeds the potential on zinc. Protection by arsenic and mercury are alike in their

nature. Tin and lead are very slowly dissolved by non-oxidising acids, although their potentials are such as would cause their ready solution in acids, if it were not for the unusually high discharge potential of hydrogen on them. Removal of hydrogen by an oxidising agent causes these metals to dissolve readily in acids that otherwise corrode them very slightly. Corrosion by acids, of metals below hydrogen in the electrochemical series, namely, copper and silver, has been brought about by the presence of oxidising agents. The statement that the corrosion of amalgamated zinc in dilute sulphuric acid is accelerated in a vacuum is shown to be incorrect. By removing the depolarising oxygen of the air, reduction of pressure retards corrosion, not only of amalgamated zinc, but of other metals the solution of which is hindered by a polarising film of hydrogen. With respect to their corrosion the metals examined may be classified as follows: (*a*) Metals the potentials of which exceed the discharge potential of hydrogen on them; these dissolve readily in acids except such as form insoluble salts. (*b*) Metals the potentials of which are less than the discharge potential of hydrogen on them; these dissolve readily in acids only in the presence of oxidising agents. Gold and platinum are not readily attacked by acids in general, even when these contain oxidising agents. The superiority of nitric acid over other acids as a solvent for metals is due to its being at the same time an acid and an oxidising agent, which enables it to dissolve metals of the second class, which non-oxidising acids are unable to do. Oxygen is necessary for success in cyaniding gold ores because in dilute cyanide solutions gold is a metal of the second class. Measurements of the discharge potential of hydrogen in solutions of potassium cyanide and sodium hydroxide, and experiments on the corrosion of metals in the latter, lead to the conclusion that the above classification, the action of oxidising agents, and protection by other metals will apply to the dissolving of any metal in any electrolyte from which it displaces hydrogen when passing into solution. The above classification of metals according to the relative magnitude of their potentials in comparison with the discharge potential of hydrogen on them applies not only to the solution of metals, but also to their electrolytic deposition. Plating baths for depositing metals of the first class cannot be strongly acidified without causing the deposition of much hydrogen in place of an equivalent amount of metal; but a large proportion of acid may be added to solutions for the deposition of metals of the second class without greatly lowering the current efficiency through the deposition of hydrogen. J. F. S.

Heat of Hydration of Gaseous Atomic Ions. K. FAJANS (*Ber. Deut. physikal. Ges.*, 1919, **21**, 709—713. Compare this vol., ii, 12, 21).—A theoretical paper in which a correction of the heat of hydration of the hydrogen ion is made; in place of the previously published figure $H^{\cdot}=362$ Cal. per gram ion, the more correct, but still approximate, value 260 Cal. per gram ion is substituted. The term "hydration of ions" is more fully defined.

The term is not intended to indicate the formation of hydrates of the ions of definite stoicheiometric composition, but rather that, due to the electrostatic charge of the ions, the oppositely charged part of the polar water molecule is turned toward the ion, and this in its turn exerts an attractive force on the next molecule. This type of dielectric polarisation proceeds continuously in the water surrounding the ion. The heat of hydration increases with decreasing volume of the gaseous ion, and reaches an exceedingly large value with the hydrogen ion. J. F. S.

Affinity of Halogen Atoms for Electrons and the Energy of Ionisation of the Hydrogen Haloids. K. FAJANS (*Ber. Deut. physikal. Ges.*, 1919, **21**, 714—722. Compare preceding abstract).—A theoretical paper in which, making use of the principles previously published, the author calculates the energy change, in the form of a development of heat, which results from the combination of the halogen atoms with an electron. It is shown that the combination occurs with considerable loss of energy, but that the amount decreases with increasing atomic weight; the values found are in Cals.: chlorine 116, bromine 87, and iodine 81. The wave-length of the spectrum line brought about by this combination is calculated by means of the formula $\epsilon = h\nu = h \times 3 \times 10^{10}/\lambda$, in which ϵ is the energy change and λ the wave-length in Ångström units. The following values are obtained: chlorine 2440, bromine 3350, and iodine 3490. By the same method of calculation, the work of ionisation of the hydrogen haloids has been obtained. The heat of combination of a gaseous hydrogen ion with a gaseous halogen ion is found to be: chlorine 322, bromine 310, and iodine 300 Cal. Using the formula $V = 1000U/96{,}500 \times 0{\cdot}2388$, in which V is the ionisation potential and U the energy change, the ionisation potential has been calculated, and the following values obtained: hydrogen chloride 14·0 volts, hydrogen bromide 13·4 volts, and hydrogen iodide 13·0 volts. J. F. S.

Electron Affinity of Gases. K. FAJANS (*Ber. Deut. physikal. Ges.*, 1919, **21**, 723—727. Compare preceding abstracts).—In an earlier publication, Franck (A., 1910, ii, 817) attributes the loss of mobility of negative ions in the presence of oxygen and other gases to the combination of the gas atoms with electrons, and he formulates a potential series of the various gases. This question is discussed in the present paper. It is shown that the collision of an electron with a gas molecule effects the change represented by one of the equations: (1) $X_2 + \ominus = X + X^-$; (2) $X_2 + 2\ominus = 2X^-$. For the halogens, the potential of the change is calculated, and the following values obtained: equation (1), chlorine −0·44 volt, bromine −1·78 volts, and iodine −1·96 volts; equation (2), chlorine −5·47 volts, bromine −5·55 volts, and iodine −5·47 volts. In the case of the hydrogen haloids, particularly hydrogen chloride, the change $HX + \ominus = H + X^-$ is supposed to occur, and this, on calculation, yields the potentials: hydrogen chloride +0·39 volt, hydrogen bromide −0·09 volt, and hydrogen iodide −0·53 volt.

Both considerations explain the formation of gas ions from electrons and atoms without the necessity of assuming a specific electron affinity. J. F. S.

Theory of Heat Change. F. HABER (*Ber. Deut. physikal. Ges.*, 1919, **21**, 750—768).—A theoretical paper in which the author discusses the theory of heat change in connexion with (i) hydration energy of gaseous ions, (ii) energy of dissociation of salt vapours and ionisation potential of metal cations, and (iii) lattice energy and ultra-violet characteristic frequencies. J. F. S.

Affinity of the Halogen Atoms towards Electrons. M. BORN (*Ber. Deut. physikal. Ges.*, 1919, **21**, 679—685. Compare Born, A., 1919, ii, 214; Fajans, this vol., ii, 12).—A theoretical paper in which, based on the theory put forward previously by the author and Fajans (*loc. cit.*), the affinity of the halogen atoms for electrons is calculated. The values E, the energy of combination of an atom with an electron, Z, the energy of dissociation of an atom into ion and electron, and D, the heat of dissociation of a diatomic gas, are calculated, and the following numerical values in Cals. obtained: fluorine, $Z=-26$ (mean); chlorine, $Z=-62$ (mean), $D=57$, $E=119$ Cals., or 5·16 volts; bromine, $Z=-61$, $D=23$, $E=84$ Cals., or 3·64 volts; iodine, $Z=-59$, $D=18$, $E=77$ Cals., or 3·33 volts. It is shown, also, that the wave-length corresponding with the energy can be calculated on the basis of the quantum theory. The following wave-lengths in Ångström units are obtained: chlorine, $\lambda=2380$; bromine, $\lambda_E=3360$; iodine, $\lambda_E=3680$. J. F. S.

Cuprous Oxide Photo-chemical Cell. THEODORE W. CASE (*Trans. Amer. Electrochem. Soc.*, 1917, **31**, 351—364).—The action of light on one electrode of the cell $Cu|Cu_2O|$aqueous copper formate + formic acid$|Cu_2O|Cu$ has been investigated. It is found that an *E.M.F.* up to 0·085 volt can be obtained and a current of 0·003 ampere if the metal plates are 20 × 3·2 cm. in size. By arranging the cell on a rotating disk, so that the copper plates are alternately illuminated, an alternating current of various amplitudes and frequencies may be obtained. The action of the cell indicates that, under proper conditions, its life may be continuous, and that its elements will not disintegrate. The action of the cell is compared to the resistance change of the mineral cuprite when exposed to ultra-violet light. The contrast between the *E.M.F.* effect of cuprous oxide and cupric oxide is discussed. The action of the cuprous oxide photochemical cell is explained on the basis of the oxidation of cuprous oxide to cupric oxide in light. It is shown that there is no relation between the sign of the light action and the colour of heated copper plates. J. F. S.

Determination of Hydrogen-ion Concentration. JOHN W. M. BUNKER (*J. Biol. Chem.*, 1920, **41**, 11—14).—A modification of a bubbling electrode used in a closed vessel is fully described.

[he apparatus is designed to meet the requirements of quick, ccurate determinations in large numbers, and has given satisfactory esults. J. C. D.

Phenomenon after Anodic Polarisation. II. A. SMITS, G. L. C. LA BASTIDE, and TH. DE CRAUW (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 296—299. Compare this vol., ii, 8).—It vas previously shown that, on interrupting the current by which ron is polarised anodically, the potential of the iron falls, passes hrough a minimum, and then reaches the original value. This is lue to diffusion changes, which affect the ratio $Fe^{\cdot\cdot}/Fe^{\cdot\cdot\cdot}$. A imilar phenomenon is now observed for nickel which has been nodically polarised. In solutions of nickel chloride, the minimum s reached in less than three seconds, whilst in the case of nickel ulphate, the change is much more prolonged. On cathodic polarsation of iron, the reverse phenomenon is observed, namely, the otential of the iron passes through a maximum and then falls to he normal value. This is to be expected if the explanation offered 1 the case of anodically polarised iron is correct. J. F. S.

Polarisation Tension and Constitution of Complex Cobalt Compounds. NILRATAN DHAR and G. URBAIN (*Compt. end.*, 1920, **170**, 106—108).—The polarisation tension of a complex alt depends, not only on the constitution of the complex ion, but lso on the nature of the ion which accompanies it. Thus, in the ries starting with $[Co(NH_3)_6]Cl_3$, the replacement of ammonia by ater causes a diminution in the tension, whereas in the series

$$[CoCl_2(NH_3)_4]Cl$$

ie contrary holds good. The replacement of a molecule of water y a halogen in such a compound as $[Co(NH_3)_5,H_2O]Cl_3$ causes a se in the polarisation tension. Further, in the purpureo-salts, the nsion is higher when the purpureo-complex contains a more egative radicle. The replacement of a chlorine atom by a nitroroup or of two chlorine atoms by a carbonato-group causes a wering of the polarisation tension. The marked rise in the tension llowing on the substitution of an hydroxy-group for a chlorine om is in agreement with the fact that these complex compounds e only stable in alkaline media. W. G.

The Polarisation in Solutions of Iron. W. ALBERT NOYES, in. (*Compt. rend.*, 1920, **170**, 177—180. Compare this vol., , 9).—Nernst's formula, $A = 0.0002T/m_1n_1$, for calculating the alue of A in the equation $Ep = A \log_{10} I + B$, giving the potential of 1 electrode traversed by a current, does not apply to the polarsation of solutions of ferrous salts, but none the less gives values oportional to the experimental values. W. G.

Electrolytic Behaviour of Tungsten. WALTER E. KOERNER *rans. Amer. Electrochem. Soc.*, 1917, **31**, 221—255).—The otential of tungsten in *N*-solutions of potassium cyanide, sodium ydroxide, potassium hydroxide, ammonium hydroxide, sulphuric

acid, hydrochloric acid, potassium nitrate, nitric acid, potassium fluoride, potassium chloride, potassium bromide, potassium sulphate, and potassium iodide has been measured against certain standard electrodes at 25°. The results show that tungsten does not behave as an insoluble electrode, but sends ions into the solutions with velocities which vary with the different solvents. Tungsten has a lower potential in *N*-alkalis than in *N*-acids, and a lower potential in *N*-acids than in *N*-salts. The following *E.P.* values (H = 0) are calculated from the experimental results; all solutions were normal: potassium cyanide, −0·647 volt; sodium hydroxide, −0·316 volt; potassium hydroxide, −0·315 volt; ammonium hydroxide, −0·238 volt; sulphuric acid, 0·193 volt; hydrochloric acid, 0·256 volt; potassium nitrate, 0·300 volt; nitric acid, 0·311 volt; potassium fluoride, 0·522 volt; potassium chloride, 0·563 volt; potassium bromide, 0·589 volt; potassium sulphate, 0·719 volt; and potassium iodide, 0·733 volt. A further series of *E.M.F.* measurements were made for tungsten in saturated solutions of tungstic acid in *N*-solutions of hydrochloric, sulphuric, and nitric acid respectively. The following values are obtained: hydrochloric acid, 0·317 volt; sulphuric acid, 0·313 volt; and nitric acid, 0·317 volt. The following combinations were also measured:

$$W \mid W(OH)_6, N\text{-}H_2SO_4 \parallel N\text{-}H_2SO_4 \mid W,$$

0·117 volt; $W \mid W(OH)_6, N\text{-}HCl \parallel N\text{-}HCl \mid W$, 0·057 volt; and $W \mid W(OH)_6, N\text{-}HNO_3 \parallel N\text{-}HNO_3 \mid W$, 0·009 volt. The *E.M.F.* values obtained give the relative solubilities of tungstic acid in *N*-acid solutions. Analytically, the values were found to be: sulphuric acid, 0·02281 gram WO_3 per litre; hydrochloric acid, 0·01067 gram WO_3 per litre; and nitric acid, 0·00025 gram WO_3 per litre. The anodic behaviour of tungsten has been investigated, and it is shown that in solutions of tungsten in acids it behaves as a cation, whilst in solutions of tungsten in alkalis it behaves as an anion. Tungstic acid goes into solution in acids and alkalis as an electrolyte, and not as a colloid. Tungsten dissolves anodically in aqueous and non-aqueous solutions of alkalis, acids, and salts. Under specified conditions, tungsten becomes passive when used as anode in aqueous and non-aqueous solutions of acids, bases, and salts. In aqueous solutions of alkalis and non-aqueous solutions of acids, bases, and salts, tungsten only becomes passive at high current densities (2 amperes per sq. dcm.). In aqueous solutions of acids and salts, the passive condition is assumed by tungsten at low current densities, and only at extremely low current densities will it remain active in these solutions. The passivity of tungsten is due to adherent films of hydrated oxides of tungsten. The films may be readily dissolved and the passivity destroyed. The hydrated oxide films appearing on the anode vary in colour from brown through blue to yellow. The degree of passivity varies with the colour of the films. The electrochemical equivalent of tungsten was found to be 0·3173 mg. per coulomb, a value very closely in agreement with the theoretical value. A number of experiments on the use of tungsten in storage cells are recorded. It is found

that the potential difference between the brown oxide (+) and the blue oxide (−) is 0·75 volt. J. F. S.

Electrical Endosmose and Adsorption. T. R. Briggs, H. L. Pierson, and H. S. Bennett (*Trans. Amer. Electrochem. Soc.*, 1917, **31**, 257—270).—Using a modified form of Perrin endosmometer, which obviates the error produced by the evolution of gas at the electrodes and permits the use of diaphragms composed of powdered solids, the authors have determined the effect of the applied *E.M.F.* on the rate of flow of the liquid for the case of water with a glass diaphragm. In this case, the liquid flowed to the cathode, and the rate was found to be in keeping with Perrin's law for *E.M.F.* values lying between 530 and 100 volts. The effect of temperature on the rate of flow, using water and asbestos diaphragms and cellulose in boiled water, was determined at temperatures from 18° to 67°. It is shown that the product, rate × viscosity^{-4}, is practically constant. The flow of liquid in acid and alkaline solutions was investigated with alundum diaphragms, when sharp reversals were obtained, which are in keeping with Perrin's results. With glass diaphragms, no such reversal of direction was observed. The effect of barium ions on the rate of flow to the cathode in alkaline solutious is to reduce it much more than would an equivalent quantity of univalent ions. In acid solutions, barium ions have little effect, but sulphate ions reduce the rate much more than chloride, nitrate, or acetate ions. This with alundum and carborundum diaphragms. A number of experiments with dyes in *N*/500-solutions of hydrochloric acid and sodium hydroxide are described. It is shown that acid dyes (eosin, crystal ponceau) in alkali travel to the cathode, whilst basic dyes (safranine and methylene-blue) in acids travel to the cathode; acid dyes in acids and basic dyes in alkalis give indefinite results; alundum diaphragms were used in these experiments. The relationship between dyeing and electrical endosmosis tends to confirm the adsorption theory. J. F. S.

Chemistry of the Flaming Arc, in Relation to Luminescence. William Roy Mott (*Trans. Amer. Electrochem. Soc.*, 1917, **31**, 365—390).—The light produced by flaming arcs containing various substances, and the relative volatility of refractory substances have beeu investigated. It is shown that there is no case of a blue arc shell. In every case except barium and vanadium, the arc core is blue or violet and the shell green, yellow, or red. Hence the light from the shell in every case but barium and vanadium is of longer wave-length than that of the arc core. The non-metallic elements, fluorine, chlorine, bromine, iodine, oxygen, sulphur, and nitrogen do not give elemental spectra, bnt fluorine, chlorine, oxygen, and nitrogen give the spectra of compounds in a carbon arc. The elements phosphorus, arsenic, and boron give only a few ultraviolet lines in the carbon arc. The easily reduced metals except those of the iron group yield no arc shell. The low energy of reac-

tion at high temperatures explains this lack of light. The most electropositive elements give the most markedly coloured luminous shells, especially where more than one valency stage is characteristic of the element at high temperatures. With yttrium oxide, the crater on the bead alone gives a green shell, which replaces the usual red shell obtained with the crater partly on the bead and partly on the carbon. Zirconium oxide gives a yellowish-white shell. The colour is probably due to hot solids, as zirconium carbide is less volatile than platinum, and its oxidation would give an extremely non-volatile oxide. Metallic zirconium is fairly volatile. In nearly every case with a carbon arc the flow of material is from positive to negative. With mixtures of salts of potassium, rubidium, and cæsium fluoride respectively with calcium fluoride a strong blast also comes from the negative crater which causes a unique dimness near the negative part of the arc. A dim, large positive crater can often be produced by nearly all salts of potassium, rubidium, and cæsium and by oxy-salts of sodium. This, with the effect on cyanogen bands and arc length may be explained by the reaction $KF + C_2N_2 = KCN + CNF$, and others necessary to return by oxidation to potassium fluoride, carbon dioxide, and nitrogen. A dim negative crater is most easily produced by barium salts volatilised from the positive crater. Glucinum oxide is the least volatile of the oxides which are so insulating as to prevent cratering, such as oxides of the alkaline earths, aluminium oxide and silica. The oxides of yttrium, zirconium, thorium, and the other rare earths allow cratering. Tungsten is by far the least volatile of the known elements, and this is followed by tantalum. The light of a yellow flame arc is due to reactions involving calcium fluoride, calcium oxide, calcium carbide, and metallic calcium.

J. F. S.

Magnetism of the Metalammine Compounds. ERNST ROSENBOHM (*Zeitsch. physikal. Chem.*, 1919, **93**, 693—720).—The magnetic susceptibility of a very large number of metallic ammine derivatives has been determined at 16—20° by means of a Curie torsion balance. The metals investigated were cobalt, platinum, rhodium, iridium, ruthenium, zinc, nickel, copper, and chromium. The ammine derivatives of cobalt, platinum, iridium, rhodium, zinc, and ruthenium are, except in the case of some of the cobalttriammines, diamagnetic. The diamagnetism is greatest in hexammine salts of cobalt, somewhat less in the pentammine derivatives, very much less in the tetra-ammine derivatives, and least in the triammine derivatives of cobalt. In the last class of compounds it is found occasionally that paramagnetism is exhibited. The same regularity is observed when the whole or a portion of the ammonia group is replaced by ethylenediamine or propylenediamine. The entrance of one or more ionogen residues iuto the sphere of the metallic atom is shown to be followed by a decrease in the diamagnetism in the case of all the diamagnetic metallic ammiues investigated. In the case of platinum it is shown that the susceptibility and molecular magnetism of

bivalent platinum is less diamagnetic than is the case with quadrivalent platinum. Further, as in the case of the electro-conductivity, in passing from hexammino- to hexacido-derivatives, the magnetism passes through its extreme value with those compounds which have no ionogen acid residue. The ammine derivatives of nickel, copper, and chromium are paramagnetic. In the case of the chromium derivatives it is shown that the magnetic susceptibility and the molecular magnetism are least in the hexammine derivatives and increase steadily to the triammine derivatives. As in the case of the cobalt derivatives the extreme value occurs with those derivatives which contain no ionogen acid group. The examination of the geometrical isomerides of the derivatives of cobalt, platinum, and chromium indicates that magnetically the *cis*- and *trans*-forms of a given compound cannot be differentiated. At the same time it is shown that the measurement of the magnetic susceptibility is a very sensitive method of testing the purity of these isomerides. In the case of the optical isomerides of cobalt and chromium, it is shown that the *d*- and *l*-forms have the same susceptibility, whilst the racemate has a different value. In most cases the susceptibility of the racemate is smaller than that of the active isomerides, but this is not always so. In the case of the co-ordination isomerides of cobalt and chromium, it is found that the susceptibility is not alike, but in most cases the two values are not very different. The greatest difference is found in the case

$$[Cr(NH_3)_6][Co(C_2O_4)_3]\chi\cdot 10^6 = 18{\cdot}80;$$

$[Co(NH_3)_6][Cr(C_2O_4)_3]\chi\cdot 10^6 = 13{\cdot}75$. The difference observed between the co-ordination isomerides and the other types of isomerides is probably due to the fact that the two nucleus atoms are magnetically opposed to one another, the one acting diamagnetically and the other paramagnetically. An examination of the magnetic influence of the nucleus atom shows that metalammines, with a metal valency which is stable in the normal salts, possess a susceptibility of the same order as the normal salts, whilst metalammines, with a metal valency which is unstable in the normal salts, may have a susceptibility very different from that of the normal salts, and it may even be of the opposite sign. Measurements of the polynuclear cobalt and chromium ammines show that these compounds are quite normal in their magnetic relationships. The molecular magnetism is calculated from Pascal's formula, $M = \Sigma A + 1$ (A., 1911, ii, 91), and the values compared with the present measurements. It is found that both sets of values are remarkably close. The magnetic properties are considered in connexion with the magnetone, and it is shown that in accordance with Weiss's theory the magnetone number is always a whole number. J. F. S.

A Thermoregulator with the Characteristics of the Beckmann Thermometer. R. B. HARVEY (*J. Biol. Chem.*, 1920, **41**, 9—10).—The instrument can be set easily at any temperature desired between $-20°$ and $+250°$. The electrical contacts are placed so that small temperature changes will make or break the circuit. When run on test in an air-bath with a standard Beckmann

thermometer and vigorous stirring, the air temperature was regulated to within $\pm 0.004°$. J. C. D.

Specific Heat of Sulphuric Acids, Nitric Acids, and their Mixtures. PAUL PASCAL and M. GARNIER (*Bull. Soc. chim.*, 1920 [iv], **27**, 8—18).—*Using an electrical method of heating*, the authors have determined the specific heats of binary mixtures of sulphuric acid and water containing from 10 to 100% of sulphuric acid, of binary mixtures of nitric acid containing from 10 to 98% of nitric acid, of binary mixtures of nitric and sulphuric acids, and of ternary mixtures of nitric and sulphuric acids and water. The results are set out in detail, and a graph with trilinear co-ordinates combines the data. W. G.

Latent Heat and Surface Energy. G. RUDORF (*Phil. Mag.*, 1920, [vi], **39**, 238—239).—*A criticism of Hammick's paper under* the above title (A., 1919, ii, 389), in which it is shown that using more accurate values for γ (surface tension), σ (molecular diameter), and L_i (internal latent heat), the values of $\gamma V/J\sigma$ and $L_i/6$ give results which are widely divergent in the case of argon. The values calculated by the author are 302 and 240 respectively, instead of 226 and 214 calculated by Hammick. J. F. S.

Critical Constants. Critical Temperature of Hydrogen Bromide. E. MOLES (*J. Chim. Phys.*, 1919, **17**, 415—424). —A criticism of Fielding's work (compare A., *1919*, ii, 45) in which the author supports the law of Guldberg and Guye as to the relationship between the absolute critical temperature and the absolute boiling point/760 mm.

For hydrogen bromide the author finds experimentally the value 89·80° for the critical temperature, and the value as calculated by Guldberg and Guye's rule is in reasonably close agreement with this.

He further indicates that Fielding's formula (*loc. cit.*) for calculating the critical pressure gives results considerably higher than those found by experiment in the cases of hydrogen chloride and hydrogen sulphide. W. G.

Form and Regularities of the Vapour Pressure Curve. E. WERTHEIMER (*Ber. Deut. physikal. Ges.*, 1919, **21**, 692—708).— A theoretical paper in which it is shown that the previously published vapour-pressure formula, $p+Ap^2=CT^n$ (*ibid.*, 1919, **21**, 435), contains in itself five approximation laws dealing with the saturation state, namely, Dühring's rule of constant boiling-point difference, the law of analogous state, Trouton's rule of normal heat of vaporisation, the constancy of the van der Waals' number (f) at the critical point, and the Nernst equation for calculating chemical constants. These expressions are all developed from the above formula, and examined by means of a large number of previously published examples. J. F. S.

Vapour Pressure Regularities. W. Herz (*Zeitsch. Elektrochem.*, 1919, **25**, 408—409. Compare A., 1919, ii, 218).—According to the theory of corresponding states, the proportionality factor a in van der Waals's equation, $\log \pi_0/p = a(\delta_0/T - 1)$, where π_0 is the critical pressure, δ_0 the critical temperature (in absolute units), and p and T corresponding values of pressure and temperature, should for all normal substances have the constant value 3. The value of a has been calculated for the elements hydrogen, nitrogen, oxygen, mercury, argon, krypton, xenon, chlorine, and bromine, and in most cases it is nearer 2 than 3, and is always less than 3. In vertical series the value increases with the atomic weight of the element. The value of the constant has also been calculated for the hydrocarbons pentane to decane, acetic and propionic acids, a number of alkyl esters of fatty acids, and some alkyl chlorides, in some cases for a number of different temperatures. In all these cases its value is close to 3. It may rise or fall with increasing temperature, and in most cases shows a distinct rise as a homologous series is ascended. Associated liquids show a greater value for a than similarly constituted non-associated liquids. Thus the value for water is greater than that for hydrogen sulphide, and that for ammonia greater than that for phosphine. E. H. R.

Relative Volatilities of Refractory Materials. Wm. Roy Mott (*Trans. Amer. Electrochem. Soc.*, 1918, **34**, 255—295).—Ten arc methods of ascertaining the relative volatilities of metals, carbides, oxides, nitrides, fluorides, chlorides, and sulphides are suggested and to some extent developed. The most rigid method depends on the least volatile material remaining as the residue when distilling mixtures. For materials boiling above the boiling point of iron saturated with carbon (3500°) a series of boiling points has been estimated on a triple basis of reference, namely, reference to the curves for iron for equal atomic amounts of material, fractional distillation series, and position of deposition at the negative arc crater. The boiling points in the series are: iron saturated with carbon, 3500°; silica, 3500°; palladium, 3600°; carbon, 3700°; alumina, 3700°; chromium carbide, 3800°; vanadium carbide, 3900°; rhodium, 4000°; platinum, 4050°; uranium carbide, 4100°; ruthenium, 4150°; lanthanum oxide, 4200°; titanium carbide, 4300°; yttrium oxide, 4300°; columbium carbide, 4300°; zirconium oxide, 4300°; thorium oxide, 4400°; iridium, 4400°; osmium, 4450°; molybdenum carbide, 4500°; yttrium carbide, 4600°; thorium carbide, 5000°; zirconium carbide, 5100°; tantalum carbide, 5500°; tungsten carbide, 6000°. Tungsten allows carbon to distil rapidly through its molten carbide, which probably surrenders carbon vapour exactly as copper oxides surrender oxygen. The boiling point of tungsten is estimated at 6000° and that of tantalum at 5500°. Zirconium carbide is the least volatile carbide, and is followed by thorium carbide. Thorium oxide is the least volatile oxide, whilst the white and yellow oxides of zirconium are nearly as non-volatile. The least volatile non-cratering oxide is glucinum oxide (b. p. 3900°), which is left as a final residue in fractional

distillation of its mixtures with barium oxide, strontium oxide, calcium oxide, magnesium oxide, silica, and alumina. From the crater distances at positive and negative, the boiling points of the more common refractory oxides are estimated as follows: barium oxide, 2000°; titanium oxide, below 3000°; chromium sesquioxide, 3000°; calcium oxide, 3400°; silica, 3500°; magnesia, 3600°; alumina, 3800°; and glucinum oxide, 3900°. "Smoke time" estimates of boiling points are given for several oxides, sulphides and halogen salts. The figures are only roughly approximate. The volatility of oxides follows the increasing order: potassium, sodium, lithium, vanadium, boron, barium, strontium, manganese, iron, cobalt, nickel, chromium, titanium, silicon, calcium, magnesium, aluminium, erbium, cerium, neodymium, lanthanum, zirconium, and thorium. The characteristic oxide is intended in every case. Boron nitride sublimes at about 3000°. As an addendum to the paper is added a bibliography of work on the volatilisation of refractory materials, and where in these papers figures are given for boiling points and melting points these are recorded. A further addendum deals with the ratio of the melting point to the boiling point. These values are given for practically the whole of the elements, and it is shown that with the exception of the metals of the first group of the periodic system the ratio abs. b. p./abs. m. p. = *ca.* 1·8. J. F. S.

Glass Rectifying Column especially suitable for the Rectification of Liquid Mixtures and the Recovery of Volatile Solvents. W. ELSNER (*Chem. Zeit.*, 1920, **44**, 11—12).—The apparatus consists of a glass column 50 mm. in diameter and filled with glass balls, the surfaces of which are ground or etched. A perforated plate at the bottom of the column serves as a support for the balls, and the latter are of three sizes, the lower part of the column containing the largest balls, whilst the smallest balls form the uppermost layers. The top of the column is connected with a small glass dephlegmator provided with a water jacket, which is supplied from a constant-level reservoir, and above the dephlegmator is a still-head carrying a thermometer and a side-tube, which is connected with a condenser. All parts of the apparatus are connected together by means of ground-in joints. W. P. S.

Saturation Pressure, calculated from the Temperature, Latent Heat of Vaporisation, and the Molecular Volume of the Liquid by means of Maxwell's Distribution of Velocities Law. K. K. JÄRVINEN (*Zeitsch. physikal. Chem.*, 1919, **93**, 743—753).—A theoretical paper wherein equations are deduced by means of which the saturation pressure may be calculated. These equations have the form

$$c_2 = c_3/c = \sqrt{(2W_i + 3RT)/M} : \sqrt{3RT/M} = \sqrt{(2W_i/3RT) + 1},$$

and $z = p/p_a$, in which z is the number of molecules which have a velocity c, c_2 is the mean velocity of the molecules, p is the

saturation pressure, p_a the internal pressure, and W_i the internal latent heat of vaporisation. The remaining symbols have their usual significance. The expression has been tested on the substances oxygen, nitrogen, benzene, ether, *n*-pentane, toluene, and methyl butyrate, and a fair agreement with fact obtained.

J. F. S.

Molecular Attraction. IV. K. K. Järvinen (*Zeitsch. physikal. Chem.*, 1919, **93**, 737—742. Compare preceding abstract, and A., 1913, ii, 293; 1915, ii, 251; this vol., ii, 90).—A theoretical paper in which the author recalculates the constants used in the formulæ previously published (*loc. cit.*). It is found for monatomic molecules that $n=5$ and $a=55{\cdot}06 \,.\, W_i \,.\, v^{\frac{1}{3}}=41{\cdot}30 \,.\, C_a v^{\frac{1}{3}}/a$. In the case of polyatomic molecules, the molecular attraction is represented by the expressions $F=m^2k/(r-\beta r_0)^n=m^2k/(v^{\frac{1}{3}}-\beta v^{\frac{1}{3}})^n$. From this equation, the following expressions are deduced:

$$a=(n-1)/3 \,.\, W_i(v^{\frac{1}{3}}-\beta v_0^{\frac{1}{3}})^{n-1}=Ca(v^{\frac{1}{3}}-\beta v_0^{\frac{1}{3}})^n/v^{\frac{1}{3}} \,.\, a$$

and $C_a/a \,.\, W_i=(n-1)/3 \,.\, v^{\frac{1}{3}}/(v^{\frac{1}{3}}-\beta v_0^{\frac{1}{3}})$. In these expressions, the symbols have the meaning previously applied to them, r_0 is the smallest distance between the molecules, and v_0 the smallest volume; $n=5$ and $\beta=0{\cdot}242$, whence $C_a/a \,.\, W_i=4/3\times 1{\cdot}27=1{\cdot}69$. A number of substances on which the formulæ have been tested give the constant 1·69, and agree most nearly with the value $n=5$. J. F. S.

Method of Calculating the Limits in Physico-chemical Phenomena. Maurice Prud'homme (*J. Chim. phys.*, 1919, **17**, 377—382).—The method previously employed for calculating the critical temperature in terms of the surface tension (compare A., 1919, ii, 183) is shown to be applicable for calculating the density at absolute zero as a function of the temperature in the case of gases, and it is shown that, as in the case of liquids, the density at absolute zero is four times the critical density. The critical pressure may also be calculated as a function of the temperature, subject to a correction of 8°, the calculated value being too high. W. G.

Molecular Condition of Liquids and Solutions. Ernst Kröber (*Zeitsch. physikal. Chem.*, 1919, **93**, 641—692).—Density determinations have been made at 25° of a large number of solutions of liquids in organic solvents, and of a number of solid substances in solid solvents. The number of molecules of solvent replaced by one molecule of the dissolved substance in unit volume is calculated in each case. It is shown that the number of replaced molecules is approximately equal only when the dissolved substance belongs to a closely related group, for example, the mono-substitution derivatives of benzene. In all other cases, different numbers of molecules of the solvent are replaced; the respective figures are approximately in the same proportion as the molecular volumes, and the relationship is only slightly dependent on the nature of the solvent and the concentration of the dissolved substance. The behaviour of solutions of solids at various temperatures has been

investigated. The volume changes accompanying the solution of liquids is small, and is not specific either in the case of solvent or dissolved substance. In the case of solids dissolved in liquids, the positive volume changes are larger, and in general appear to be due to a change in the state of aggregation. In most cases, a characteristic behaviour is observed, both with the solvent and the dissolved substance. The coefficient of compressibility and the coefficient of expansion run parallel with the mean atomic concentration and the reciprocal of the mean atomic volume. In homologous series, the atomic concentration, corresponding with constant atomic volume, is nearly constant at the boiling point, and for all substances which contain only carbon, hydrogen, and oxygen the value fluctuates only between very narrow limits. It appears possible, from the properties of a mixture, particularly from the coefficient of expansion, to decide whether a contraction or an expansion will take place. In the very large number of cases examined, only three cases were exceptional to the rules formulated, and in all probability these cases were abnormal, because of a chemical reaction between the components. J. F. S.

Viscosity Measurements. O. FAUST (*Zeitsch. physikal. Chem.*, 1919, **93**, 758—761).—The influence of the diameter of the tube on the viscosity of liquids has been investigated in connexion with the method of viscosity measurements made by determining the time required for a bubble of air to rise through a measured length of the liquid. It is shown that $Q=\pi(r^2-r_1^2)$, in which r is the radius of the tube, r_1 the radius of the air bubble, and Q the cross-section of the liquid between the bubble and the tube. Since $(r-r_1)$ is constant and $r+r_1 \simeq 2r$, $Q=2\pi r\times C$, where C is a constant. The formula is tested with a viscid oil with tubes of various diameters, and the measured time compared with the calculated time. It is shown that with wider tubes (18—24 mm.) the calculated and observed results agree, but with narrower tubes (16—12 mm.) there is an increasing divergence with decreasing diameter. This is due to the fact that the error introduced by placing $r+r_1=2r$ is greater in the case of narrow tubes than in the case of wider tubes. It is also shown that in the case of wider tubes, the time required for the ascent of the bubble is independent of the size of the hubble, whilst the same is almost true with narrower tubes. J. F. S.

The Welding of Solid Powders under Pressure. TONI VON HAGEN (*Zeitsch. Elektrochem.*, 1919, **25**, 375—386).—An extensive series of experiments is described on the cohesive properties of pure powdered inorganic substances under pressure. The substances examined include the oxides, sulphides, sulphates, halogenides, nitrates, and carbonates of many metals, including both anhydrous and hydrated forms of the salts. Fine-grained particles were found to cohere better than coarser, and for most experiments the substance was ground to pass a sieve of 25 meshes per sq. mm. The

powder was subjected, for most experiments, to a pressure of 560 kilos. per sq. cm. in a screw press, and the tablets formed were examined by inspection, and, where possible, by determining their hardness or crushing strength. The substances showing the best cohesion gave tablets which appeared homogeneous. Among these were the halogenides of the alkali metals and silver and hydrated calcium chloride. The next class gave tablets with smooth surfaces and pulverulent bodies, this class including the hydrated sulphates of aluminium, zinc, cobalt, and sodium, many nitrates and sulphides, and the oxides of lead. Most of the oxides gave powdery bodies of low crushing strength, whilst the anhydrous sulphates of potassium, calcium, strontium, barium, and lead, and the carbonates of cadmium, barium, and lead showed no cohesion at all. Generally, substances of very high melting point and very hard substances show little cohesion. A cohesive substance mixed with a non-cohesive substance improves the binding properties of the latter, but quantitative experiments on the hardness of mixed tablets showed that this was not proportional to the composition. In the case of cohesive substances, increasing pressure increases the density of the tablet, rapidly at first, then slowly as the maximum is approached. The maximum may rise to the true density of the crystalline substance, as in the case of gypsum, or it may approach very nearly to this value, as with sodium and potassium chlorides.

The experiments show that there is a close relation between the crystalline form of a substance and its behaviour under pressure. Those substances which give the most homogeneous bodies under pressure are those which have plastic crystals, that is, the crystals of which contain glide-planes and are deformable without losing their structure. The above substances, which give, under high pressure, tablets having almost the maximum possible density, have been shown to have plastic crystals. On the other hand, the crystals of such substances as quartz and barium sulphate show no trace of plasticity, and their powders show no cohesive properties. [See also *J. Soc. Chem. Ind.*, 1920, 189A.] E. H. R.

Absorption of Gases by Charcoal. I. Variations due to Heat Treatment, Pre-equilibrium Effects. HARVEY B. LEMON (*Physical Rev.*, 1919, **14**, 281—292).—The rate at which coconut-shell charcoal absorbs air, and the total amount it can absorb, may be widely varied by varying the heat treatment. This paper considers the case in which the mass of air used is less than that required for saturation. Increase in activation is produced by repeated exhaustions at 650°, each exhaustion being followed by an absorption of air at the temperature of liquid air. Decrease in activation results if a temperature of 800—900° is used. Two hypotheses to account for this, (1) the clogging of the pores by heavy hydrocarbons, removed by flushing out with gas, and (2) the alteration in the fineness of the carbon from the point of view of a saturated solution of carbon in liquid gas, are discussed, but found inconclusive, particularly inasmuch as removal of the heavy hydro-

carbons by light petroleum, alcohol, and acetone causes loss in efficiency. CHEMICAL ABSTRACTS.

Absorption of the so-called Surface Active Substances by Various Absorbents. LEONOR MICHAELIS and PETER RONA (*Kolloid Zeitsch.*, 1919, **25**, 225—229).—Comparative absorption experiments have been carried out with charcoal, kaolin, osmosil (a commercial silicic acid preparation), talc, amorphous silicon, ferric hydroxide, freshly precipitated manganese dioxide, calomel, barium sulphate, and calcium carbonate as absorbents for acetone, tributyrin, heptyl alcohol, and octyl alcohol. It is shown that no carbon-free absorbent has a power of absorption that even approaches the absorptive power of charcoal for surface active non-electrolyte substances. In most cases there is no absorption, in others only the merest trace of absorption takes place. Talc comes next to charcoal in its absorption of these substances. J. F. S.

Osmosis and Diffusion of Ions through a Polarised Septum. Physical Methods for the Study of Cellular Nutrition. PIERRE GIRARD (*J. Chim. Phys.*, 1919, **17**, 383—408).—A résumé of work already published (compare A., 1908, ii, 456; 1909, ii, 463, 537; 1911, ii, 860; 1914, ii, 718; 1919, i, 419, 461) and a reply to Hamburger (compare A., 1917, ii, 562). W. G.

Theory of Solution and Suspension. RICHARD ZSIGMONDY (*Kolloid Zeitsch.*, 1920, **26**, 1—10).—A theoretical paper in which the significance of the terms "solution" and "suspension" is discussed at length. J. F. S.

Physical Chemical Analysis of Metallic Oxide Sols. WOLFGANG PAULI (*Kolloid Zeitsch.*, 1920, **26**, 20—23).—Polemical. An answer to Zsigmondy's theory of solutions and suspensions (preceding abstract), which is based on the work of Pauli and Matula (A., 1917, ii, 563). J. F. S.

Nomenclature of Colloids. G. WEISSENBERGER (*Kolloid Zeitsch.*, 1919, **25**, 230).—The author points out that the term "gel" is applied both to jellies and to the products of coagulation. He suggests that the term gel should be retained and used only in connexion with jellies, and that the products of coagulation should be termed *coagels*, thereby implying that they belong to the group of coarse, disperse colloids. J. F. S.

Rôle of Valency in Coagulation by Electrolytes, particularly in the Case of the Suspensoids. WOLFGANG OSTWALD (*Kolloid Zeitsch.*, 1920, **26**, 28—39).—A theoretical paper in which the various views put forward in connexion with the part played by the valency of the electrolyte ions in the coagulation of colloids is critically discussed. J. F. S.

Coagulation of Clay and the Protective Effect of Humic Acid. SVEN ODÉN (*J. Landw.*, 1919, **67**, 177—208).—An extensive review is given of previous work on clay suspensions as regards their aggregation, sedimentation, disintegration, swelling value, and nature of individual particles. Experiments were made by the author with suspensions of two clays of different character, purified by dialysis, and diluted with conductivity water to about 1% strength. Varying amounts of colloidal humic acid were added to 10 c.c. of each suspension, and the effect on coagulation noted. It was found that the minimum amount required to produce a protective effect on the addition of ammonium nitrate solution as coagulant was 0·065 mg. in one case and 0·14 mg. in the other. On varying the coagulant, it was found that much larger amounts of humic acid were required to prevent coagulation with barium nitrate and cæsium chloride than with ammonium nitrate and lithium chloride. The author concludes that the protective effect of humic acid is of the same order as that of other colloids, but that it is greatly affected by the electrolyte concentration, owing to the extreme sensitiveness of colloidal humic acid to electrolytes. The effect appears to be specific for different clays and electrolytes, so that a proper explanation of the effect is still uncertain. It is clear, however, that it depends on an absorption of the protective substance by the particles to be protected. J. H. J.

Non-, Uni-, and Bi-variant Equilibria. XIX. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 318—322. Compare A., 1917, ii, 454).—A further theoretical paper dealing with the conditions of equilibrium in non-variant, uni-variant, and bi-variant systems. The present paper deals with the equilibria of n components in $n+1$ phases. J. F. S.

Characteristic Case of Rhythmic Crystal Arrangement. M. HOFSÄSS (*Zeitsch. physikal. Chem.*, 1919, **93**, 754—757).—A few drops of the $N/10$-sodium hydroxide which had been used to absorb the carbon dioxide produced in the combustion of artificial graphite was allowed to evaporate on a microscope slide. The crystals formed, when magnified 500 times, showed a striking rhythmic, concentric arrangement. Each series of rings commences from a crystal nucleus, around which circles of crystals 0·002 mm. apart are formed. In all other cases of combustion of coal, lignite, and wood, the crystals produced from the sodium hydroxide wash-bottle exhibited the usual dendritic forms. J. F. S.

The Rate of Decomposition of Malonic Acid. CYRIL NORMAN HINSHELWOOD (T., 1920, **117**, 156—165).

Mechanism of the Addition of Hydrogen to Unsaturated Glycerides in the Presence of Finely Divided Nickel. R. THOMAS (*J. Soc. Chem. Ind.*, 1920, **39**, 10—18T).—The rate of hydrogenation of olive oil (iodine value, 86) by means of hydrogen

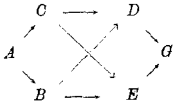
in the presence of finely divided nickel has been determined at 120°, 150°, and 180°. As the olive oil contained 7% of linolin, equations are deduced for the rate of addition of hydrogen by mixtures of unsaturated glycerides. The reaction between pure hydrogen at constant pressure and a single unsaturated glyceride takes place according to the equation for reactions of the first order. The more highly unsaturated glyceride linolin absorbs hydrogen very much faster than olein. The rôle played by the catalyst is discussed from the results of experiments on the influence of pressure of hydrogen and of temperature on the velocity of reaction. It is found that the rate of saturation of olein (with three double bonds) is proportional to $p^{\frac{1}{2}}$, where p is the pressure of hydrogen. This is in keeping with the view that hydrogen becomes active through its absorption by the catalyst, with a dissociation of the hydrogen molecules into atoms. The temperature-coefficient of the velocity constant is small; an increase of 10° in temperature over the range 120—180° increases the velocity 1·13 times. This suggests a photochemical reaction, the molecules of olein being brought into an active condition by absorption of infra-red radiation emitted by the catalyst. The mode of action of gaseous catalyst poisons is illustrated and discussed. Such action may be a purely physical one, or it may be chemical in the sense that the poison is capable of reacting either with or in the presence of the catalyst.

J. F. S.

Hydrolysis of Esters of Polyhydric Alcohols. EIICHI YAMAZAKI (*J. Tokyo Chem. Soc.*, 1919, **40**, 498—514).—Denoting the five mono-, di-, and tri-acetins by

(*A*) $OAc \cdot CH_2 \cdot CH(OAc) \cdot CH_2 \cdot OAc$,
(*B*) $OAc \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OAc$, (*C*) $OH \cdot CH_2 \cdot CH(OAc) \cdot CH_2 \cdot OAc$,
(*D*) $OH \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OAc$, and
(*E*) $OH \cdot CH_2 \cdot CH(OAc) \cdot CH_2 \cdot OH$,

glycerol (*G*) is obtained from triacetin by hydrolysis along the following routes (annexed formula).



This apparently complicated system of hydrolysis of triacetin can be studied in a simple manner, since all esters containing R·CO·O· have approximately the same constant of velocity of hydrolysis, which is independent of the position of the acid group in the polyhydric alcohol. The constants of velocity of hydrolysis of tri- to di-acetin ($K_1 = 0·00638$) and of di- to mono-acetin ($K_2 = 0·00423$) by hydrochloric acid, calculated from Geitel's data (A., 1897, ii, 547; 1898, ii, 330), are compared with the velocity constant ($K_3 = 0·002213$) for monoacetin ⟶ glycerol. Assuming that each acetoxy-group is hydrolysed at the same rate, $K_1/3 = K_2/2 = K_3 (= K)$. The following equations are thus derived: $c_{M_1} = c_0 e^{-3Kt}$; $c_{M_2} = 3c_0(1 - e^{-Kt})e^{-2Kt}$; $c_{M_3} = 3c_0(1 - e^{-Kt})^2 e^{-Kt}$; and $c_{M_4} = c_0(1 - e^{-Kt})^3$, where the concentrations of the three acetins and of

glycerol are denoted by c with suffixes M_1, M_2, M_3 and M_4 respectively. If free acetic acid is denoted by c_A, then

$$c_A = c_{M_2} + 2c_{M_3} + 3c_{M_4} = 3c_0(1 - e^{-Kt})^3.$$

A satisfactory agreement is recorded between the calculated and the observed values of c_A at any instant. CHEMICAL ABSTRACTS.

The Factors of Diazotisation. E. TASSILLY (*Bull. Soc. chim.*, 1920, [iv], **27**, 19—33).—Using the method previously described (compare A., 1914, ii, 256), the author has studied the rate of diazotisation of a number of amines. The reaction has been previously shown to be bimolecular. Doubling the acidity of the solution does not modify the process of diazotisation in the case of aniline. The diazotisation of sulphanilic acid is much more rapid when the concentration of the reacting solutions is increased, and it is favoured by an excess of sodium nitrite. The stability of a diazo-compound with respect to time and temperature may be studied by this method. W. G.

Colour Change of Congo-rubin under the Influence of Reactions and Neutral Salt Action. HEINRICH LÜERS (*Kolloid Zeitsch.*, 1920, **26**, 15—20).—The time required by solutions of congo-rubin (0·01%) to change from red to the intermediate colour between red and blue in the presence of hydrogen ions of various concentrations and in the presence of neutral salts has been determined. It is shown that with $H^{\cdot} = 5{\cdot}5 \times 10^{-5}$ the change is instantaneous, but with decreasing hydrogen-ion concentration the time increases rapidly until, with the value $H^{\cdot} = 6{\cdot}8 \times 10^{-6}$, it is practically infinite. In the presence of a neutral salt (KCl) very small hydrogen-ion concentrations cause the change to take place very rapidly. The presence of large quantities of neutral salts increases the activity of the indicator toward hydrogen ions about seventy times. In the presence of hydroxyl ions, neutral salts decrease the activity of the indicator until, with $OH' = 10^{-2}$, it no longer undergoes the colour change. These changes are explained by a change in the condition of solvation of the indicator brought about by the electrolyte. J. F. S.

Catalysis. MATHEUS D'ANDRADE ALBUQUERQUE (*Revista chim. pura applic.*, 1918, **3**, reprint 22 pp.).—After reviewing the theories which have been formulated on the subject of catalysis, the author advances the view that catalysis is due to the formation of intermediate compounds ("catalides") as a result of residual affinity. This does not apply to cases where the intermediate compound is a salt, or to catalysis by solvents, finely divided (colloidal) metals, or organic ferments. W. R. S.

Whole Number Isotopes and Allied Phenomena. F. H. LORING (*Chem. News*, 1920, **120**, 73—77).—A theoretical paper in which the experimental evidence supporting the idea of whole number isotopes is given, together with the spectroscopic examin-

ation of isotopes. The photoelectric effect in its connexion with isotopes is discussed, as well as the cyclic evolution of elements and isotopes. A table is given in the paper indicating the percentage of higher mass isotopes of the commoner elements. The whole discussion tends to show that the whole number isotopes are a reality, and that the isotopic proportions may modify the electrical properties of the elements. J. F. S.

Deduction of the Chemical Constants of Polyatomic Gases from Planck's Theory of Probability. LÉON SCHAMES (*Physikal. Zeitsch.*, 1920, **21**, 38—39).—A mathematical paper in which a method of deducing the chemical constants of tri- and tetra-atomic gases is deduced. The results are compared with those deduced by Sackur (A., 1913, ii, 128) and Tetrode (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1167). J. F. S.

Chemical Constants; Moment of Inertia of the Molecule and the Quantum Theory of Gases. LÉON SCHAMES (*Physikal. Zeitsch.*, 1920, **21**, 39—42. Compare preceding abstract).—The chemical constant i_s and the moment of inertia $P.10^{40}=\sqrt[3]{PQR}$ have been calculated by means of the equations previously developed (*loc. cit.*) for oxygen, carbon monoxide, nitrogen, carbon dioxide, and water. The following values for the moment of inertia are obtained: oxygen, 31·2; carbon monoxide, 10·07; nitrogen, 9·91; carbon dioxide, 5·80; and water, 1·365. The results are compared with the values of other investigators, particularly those of Langen (A., 1919, ii, 183), and found to be in very good agreement. J. F. S.

A Cheap and Simple Microbalance. J. H. SHAXBY (*Proc. Physical Soc. London*, 1919, **32**, 21).—A balance for loads from 5 mg. to 5 dcg., depending on the depression of a stretched thread, is described. J. R. P.

Condensers. FRITZ FRIEDRICHS (*Zeitsch. angew. Chem.*, 1920, **33**, 29—32).—A critical discussion of the various forms of laboratory condensers which have been described in literature from the time of Liebig onwards. As regards efficiency, the screw-shaped condensing tube, with five "threads" and provided with an internal cooling jacket, gives the best results. This form of condenser is more suitable for use as a reflux apparatus than is the spiral form. W. P. S.

Inorganic Chemistry.

Oxidation of Sulphurous Acid by Ferric Salts. JULIUS MEYER (*Ber.*, 1920, **53**, [*B*], 77—78).—In Houben's recent method for the estimation of ferrous and ferric iron together in acid solutions, the assumption is made that when a ferric salt is reduced by sulphur dioxide the increased acidity corresponds with two-thirds of the acid in combination with the ferric iron, according to the equation $2FeCl_3 + SO_2 + 2H_2O = FeSO_4 + FeCl_2 + 4HCl$ (this vol., ii, 56). *It is now stated that the reduction of a ferric salt most* probably proceeds in stages; thus, first, a red ferric ferrisulphite, $Fe[Fe(SO_3)_3]$, is formed, which slowly changes in the cold, more quickly on warming, into the ferrous salt, not, however, with the production of sulphuric acid, but dithionic acid, thus: $Fe[Fe(SO_3)_3] = FeS_2O_6 + FeSO_3$. Before any increase in the acidity can take place, therefore, the dithionate must be decomposed, thus: $FeS_2O_6 + H_2O = FeSO_4 + H_2SO_3$, and it is not quite certain whether this is completed even by vigorous boiling. J. C. W.

The Advantages of the Synthesis of Ammonia at Very High Pressures. GEORGES CLAUDE (*Compt. rend.*, 1920, **170**, 174—177. Compare this vol., ii, 30).—Whereas it is necessary by the German method, working at a pressure of 200 atmos., to pass the reacting gases over the catalyst a considerable number of times, with removal of the ammonia after each passage, it is only necessary to do this three times at a pressure of 1000 atmos. Other advantages of working at the higher pressure on an industrial scale are claimed. [See, further, *J. Soc. Chem. Ind.*, 1920, 187A.]

W. G.

Formation of Free Hydrogen in the Reversed Ammonia Flame. FRIEDRICH C. G. MÜLLER (*Zeitsch. angew. Chem.*, 1920, **33**, 24).—The author finds that the products of combustion of ammonia in oxygen contain hydrogen and nitrogen in the ratio 2:3 by volume. Since the result is unaltered by cooling the flame with cold water (Raschig, A., 1919, ii, 148), it cannot be due to dissociation of ammonia. On the other hand, Raschig's assumption that the equation $2NH_3 + O_2 = N_2H_2 + 2H_2O$ represents the first stage of the reaction, followed by instantaneous dissociation of N_2H_2 and partial combustion of the hydrogen, does not account for the constancy of the proportion of hydrogen produced. J. K.

The Velocity of Oxidation of Nitric Oxide. EUGÈNE WOURTZEL (*Compt. rend.*, 1920, **170**, 229—231).—The oxidation of nitric oxide takes place according to the equation of a reaction of the third order, thus: $-dp_{NO}/dt = k(p_{NO})^2 p_{O_2}$.

The action does not undergo any marked modification when half the nitric oxide is oxidised; consequently, the exclusive and rapid

formation of nitrites or of nitrosyl sulphate observed, when the gaseous products formed at the commencement of the reaction are treated with alkali or sulphuric acid, must be due to particular conditions of absorption and not of oxidation of the nitric oxide. Nitrogen trioxide, the formation of which has previously been proved (compare next abstract), is an ulterior product of the action and not its intermediate product. The velocity of this oxidation diminishes with rise in temperature. W. G.

The Existence of Nitrogen Trioxide in the Gaseous State. EUGÈNE WOURTZEL (*Compt. rend.*, 1920, **170**, 109—111. Compare this vol., ii, 108).—By measuring the contraction produced when known quantities of nitric oxide and oxygen are mixed, the nitric oxide being in excess, the authors have shown that under a total pressure of about one-quarter of an atmosphere an almost stoicheiometric mixture of nitric oxide and nitrogen peroxide contains about 2·5% of nitrogen trioxide. W. G.

Direct Formation of Carbon Monoxide by Burning Carbon in Pure Oxygen. FRIEDRICH C. G. MÜLLER (*Zeitsch. angew. Chem.*, 1920, **33**, 36).—If pure oxygen is passed downwards through a vertical quartz tube, 25 cm. in length and not more than 13 mm. in diameter, filled with pieces of wood charcoal of the size of linseed, the gas leaving the lower end of the tube will contain 85% of carbon monoxide. The upper part of the charcoal must be heated by a burner before the oxygen is admitted, and it is essential that the combustion is allowed to proceed under reduced pressure. This is attained by connecting the lower end of the tube with a vessel filled with water and opening the tap of the oxygen reservoir so that water flows from the lower vessel at the rate of 2 litres per minute. W. P. S.

A Reaction of Potassium Anhydrotellurate. P. HULOT (*Bull. Soc. chim.*, 1920, [iv], **27**, 33).—If tellurous acid or alkali tellurites are brought to complete fusion with potassium nitrate, and the mass after cooling is extracted with water, potassium anhydrotellurate, $K_2Te_4O_{13}$, is left behind as a powder, which is insoluble in water or acids. If this powder is suspended in dilute hydrochloric acid and a few pieces of zinc are added, the salt gradually disappears and a black pulverulent powder, which is pure tellurium, is left behind. W. G.

Application of the Reduction of Potassium Anhydrotellurate by Zinc to the Treatment of Tetradymite and to the Estimation of Tellurium in this Mineral. PIERRE HULOT (*Bull. Soc. chim.*, 1920, [iv], **27**, 100—101. Compare preceding abstract).—The tetradymite is first treated with dilute hydrochloric acid to remove the calcareous gangue. The powdered material is then dissolved in hot concentrated nitric acid, the solution being evaporated to dryness and the residue fused with twice its weight of potassium nitrate. The resulting mass contains potassium

sulphate and selenate, bismuth oxide, and potassium anhydrotellurate. The sulphate and selenate are removed with boiling water, and the residue is digested with dilute hydrochloric acid, whereby the bismuth oxide is dissolved out. The residue, after washing with dilute hydrochloric acid, is suspended in the same acid and some zinc is added. The whole of the tellurium is deposited in a pure state, and may be collected, dried, and weighed after the whole of the zinc has dissolved. W. G.

Reversible Oxidation of Sodium Nitrite. C. MATIGNON and E. MONNET (*Compt. rend.*, 1920, **170**, 180—182).—Sodium nitrite, when heated in an atmosphere of oxygen at a pressure of 175 atmos. and at a temperature gradually rising from 395° to 530° during nine hours, is almost completely oxidised to sodium nitrate, the heat of formation of the nitrate being given by

$$2NaNO_2 \text{ sol.} + O_2 \text{ gas} = 2NaNO_3 \text{ sol.} + 45 \text{ Cal.}$$

The reaction is too slow to be of practical use.

Calcium nitrite may similarly be converted into calcium nitrate. W. G.

Some Properties of Sodium Nitrite. C. MATIGNON and (MLLE.) G. MARCHAL (*Compt. rend.*, 1920, **170**, 232—233).—The authors find for the m. p. of sodium nitrite 276·9° (corr.). Its heat of solution is expressed by $NaNO_2$ sol. + Aq = $NaNO_2$ diss. − 3·52 Cal. Its heat of decomposition in aqueous solution by dilute sulphuric acid is given by

$$2NaNO_2 \text{ diss.} + H_2SO_4 \text{ diss.} = Na_2SO_4 \text{ diss.} + 2HNO_2 \text{ diss.} + 2 \times 4{\cdot}6 \text{ Cal.}$$

From this equation and known data they deduce

$$HNO_2 \text{ diss.} + NaOH \text{ diss.} = NaNO_2 \text{ diss.} + H_2O + 11{\cdot}1 \text{ Cal.}$$

and

$$N \text{ gas} + O_2 \text{ gas} + Na \text{ sol.} = NaNO_2 \text{ sol.} + 88{\cdot}52 \text{ Cal.}$$

Nitrous acid resembles nitric acid in its behaviour towards the following indicators: phenolphthalein, cochineal, litmus, *p*-nitrophenol, brazilin, and iodoeosin, but decomposes others, like helianthin.

Aqueous sodium nitrite is not oxidised at 100° by prolonged contact with oxygen under a pressure of 50—55 atmos., even in the presence of a catalyst. W. G.

Ammonium Silicate. III. ROBERT SCHWARZ and RICHARD SOUARD (*Ber.*, 1920, **53**, [*B*], 1—17. Compare A., 1917, ii, 31; 1919, ii, 283).—The authors have studied the electrical conductivities of solutions of dioxodisiloxane, monosilane, and silicic acid obtained from pure and technical sodium silicate, silicon tetrachloride, and tetrafluoride in ammonia, in order to determine whether there are any indications of the existence of ammonium silicate or of different molecular complexity in silicic acid of various origins. The increment of the conductivity of ammonia solutions suggests that salt formation does take place, just as the lowering

of the conductivity of sodium hydroxide by silicic acid points to the same conclusion. The dialysis of the preparations and the technique of the measurements are described.

It was soon found that the percentage of water in the preparation had a great influence on the conductivity, partly due to the different rates at which the silicic acid entered real solution. In order to eliminate this factor, or to follow it more closely, the solutions were filtered through an ultra-filter after determining the conductivity, and the amount of silica estimated. The quotient increment of conductivity/dissolved SiO_2, $\Delta k/m = Q$, therefore affords a clue to the molecular complexity of the silicic acid. The experiments show that a decrease in the proportion of water in the dioxodisiloxane or silicic acid preparation is accompanied by a fall in the value Q, not, however, gradually, but apparently in three stages. In the case of dioxodisiloxane, the value Q is about 75 when the material contains about 4·5% of water, about 50 if the proportion of water is 2%, even though the silicic acid may imbibe more water on keeping, and about 25 if the preparation is almost dry. Similarly with the various silicic acid preparations; no matter what their origin, the nearly dry specimens give a value of about 25, and those rich in water about 75. After ignition, however, silica causes no increment in the conductivity of ammonia solutions. The different values of Q suggest, therefore, that the dissolved silicic acid exists in three forms, of molecular weights in the ratio 1 : 2 : 3. The simplest forms are derived from dioxodisiloxane or monosilane, the direct hydrolysis of the latter in ammonia solutions being the most satisfactory way of preparing ammonium silicate solutions. J. C. W.

Silver Peroxide and the Valency of Silver. H. C. P. WEBER (*Trans. Amer. Electrochem. Soc.*, 1917, **32**, 391—404).—A number of experiments are described which were designed for the preparation of salts of silver in which the metal has a valency greater than unity. Except in the case of the peroxy-nitrate, the results were negative. This compound, $2Ag_3O_4,AgNO_3$, is formed on the anode during the electrolysis of silver nitrate, but if 15—25% of nitric acid is added to the solution there is no deposit, but a brown solution is formed. This solution, on examination, is found to contain both negative and positive silver-containing ions. The valency of the silver in the oxide portion of this salt is discussed. Two formulæ are put forward for the oxide part of the salt, Ag_2AgO_4 (analogous to red lead) or $Ag(AgO_2)_2$ (analogous to magnetic iron oxide). The transference experiments show that one-third of the silver is cathodic and bivalent and two-thirds anodic and tervalent, which leads to the formula $Ag(AgO_2)_2$. This indicates that the oxide portion of the peroxy-nitrate is the silver salt of an unstable *argentic acid*, $HAgO_2$. J. F. S.

Lead Borates. H. V. THOMPSON (*Trans. Engl. Ceram. Soc.*, 1918–1919, **18**, 510—511).—The white precipitate formed by mix-

ing cold concentrated solutions of lead nitrate and borax is of indefinite composition, and does not necessarily consist of lead metaborate, $Pb(BO_2)_2,H_2O$, as stated by Rose (*Ann. Phys. Chem.*, 1833, **29**, 455). The precipitate formed by adding an excess of a solution of borax to a solution of a lead salt consists of lead metaborate, and not the polyborate, $2PbO,3B_2O_3,4H_2O$, as stated by Soubeiran (*J. Pharm. Chim.*, 1825, **11**, 31).

On boiling the metaborate with an excess of boric acid solution, no definite chemical compound is formed, in contradiction to Abegg ("Handb. anorg. Chem.," 1909, **3**, ii), who states that the compound $PbO,2B_2O_3,4H_2O$ is produced.

The author confirms a statement by Le Chatelier (*Bull. Soc. chim.*, 1899, [iii], **21**, 35) that the compound $PbO,3B_2O_3$ is formed on fusing boric acid and lead carbonate and extracting the mass with water to remove boric acid. [See also *J. Soc. Chem. Ind.* 1920, March.] A. B. S.

Behaviour of Cerium Carbide towards Nitrogen. FR. FICHTER and CHR. SCHÖLLY (*Helv. Chim. Acta*, 1920, **3**, 164—172).—The requisite finely divided cerium carbide is prepared by heating a mixture of cerium dioxide (1 mol.) and carbon (6 atoms) in a graphite tube in an electric vacuum-oven at 1600°. It is found that this material, in spite of its apparent similarity to calcium carbide, does not yield any compound with nitrogen at 1250° which contains both carbon and nitrogen, but that the carbon is replaced by nitrogen, with the formation of cerium nitride. The possibility of the formation of cyanides and cyanamides from carbides appears to exist solely in the groups of the alkali and alkaline earth metals, and not in that of the earthy metals; it does not depend on the type of the carbide, but on the nature of the metal. Cerium carbide also reacts with ammonia at 1250°, yielding the nitride, but the action is slower and less complete than when nitrogen is used. H. W.

Some Complex Compounds of Mineral Chemistry. G. URBAIN (*Bull. Soc. chim.*, 1920, [iv], **27**, 81—94).—A lecture delivered before the French Chemical Society. W. G.

Constitution of Ultramarine. LAURENZ BOCK (*Zeitsch. angew. Chem.*, 1920, **33**, 23—24. Compare A., 1915, ii, 460; 1917, ii, 475).—Experiments on the action of ammoniacal silver chloride solution on artificial ultramarines are described. It is concluded that the blue rich in silica and sulphur, and based on the formula $Al_2O_3,3SiO_2$, is a definite chemical compound containing sodium, sulphur, aluminium, and silica in definite proportions; the same is true of the blue poor in silica but rich in sulphur. Further, the ultramarines are analogously constituted to the aluminium silicates. A table is given showing the known ultramarines and their relationship to natural and artificial silicates. J. K.

Equilibrium in Blast Furnace Reactions. ERNST TERRES and AUREL PONGRACZ (*Zeitsch. Elektrochem.*, 1919, **25**, 386—407). —The equilibrium of the reaction $Fe + CO_2 \rightleftharpoons FeO + CO$ has been studied by a number of different observers, whose results show considerable divergencies. A fresh investigation has therefore been made on rather different experimental lines from those used hitherto. The reaction was studied from both sides, starting on the one hand from pure iron (iron wire or ferrum limatum) and carbon dioxide, and on the other from oxidised iron (prepared by oxidising pure iron with carbon dioxide) and carbon monoxide. The reaction was carried out in a pear-shaped glass vessel, which could be heated to any desired temperature in an electric furnace. For a full description of the special apparatus used, which embodied many devices for convenience and greater accuracy, the original must be consulted.

The usual procedure in studying such reactions as the one under consideration is to allow the reacting substances to remain in contact at the particular temperature until equilibrium is reached, and then to analyse the products. This method was used by Baur and Glaessner (A., 1903, ii, 423), who plotted the composition of the gases at the end of the reaction against the temperature and obtained two distinct curves, the one obtained from the starting materials, iron and carbon dioxide, having a well-marked minimum, and the other, from ferroso-ferric oxide and carbon monoxide, showing an equally prominent maximum. The present authors allowed the reaction to proceed for a definite time at each particular temperature, and at the end of this time the gases were analysed. The reaction was studied over the temperature range 550° to 950°. The results are plotted in the form of four curves, two showing the composition of the gas mixture after seven hours, starting from either side of the equation, the other two after sixteen hours. Each curve is a straight line, the proportion of carbon monoxide in the mixed gases increasing steadily with the temperature. All four curves converge towards a point at about 950° with about 75% of carbon monoxide, showing that in seven hours equilibrium is already attained at this temperature. The two sixteen-hour curves lie between the seven-hour curves, quite close together, and converge at about 810°, showing that at this temperature equilibrium is reached in sixteen hours. The true equilibrium curve evidently lies about midway between the two sixteen-hour curves. Contrary to the results of Baur and Glaessner, the same equilibrium point is reached from either side of the equation, and the curve shows no maximum or minimum. These results are in agreement with those obtained by Schenck and his co-workers (A., 1903, ii, 423; 1905, ii, 526; 1907, ii, 470) and by Levin (A., 1912, ii, 1176).

Very careful experiments showed that the composition of the gas phase at equilibrium depends on the quantity of the solid phase present, the proportion of carbon monoxide increasing with increasing amounts of iron. This can be explained on the assump-

tion that the ferrous oxide phase is a solid solution of two components. A method for analysing the solid phase was devised, and it was shown that this always contained ferric iron. The proportion of ferrous to ferric oxide never corresponded with the composition Fe_3O_4. It was also shown that no other constituent was present in the solid phase. The fall in pressure always observed when carbon dioxide and iron are first heated together is due, not to any chemical reaction, but to absorption of the gas by the metal. [See also *J. Soc. Chem. Ind.*, 1920, 193A.] E. H. R.

Behaviour of Iron in Contact with Sulphuric Acid. C. E. FAWSITT and A. A. PAIN (*J. Proc. Roy. Soc. N.S. Wales*, 1918, **52**, 396—405).—Differences in electrochemical behaviour show that no real similarity exists between iron which is slowly dissolving in concentrated sulphuric acid and iron rendered "passive" by dipping into nitric acid. The slowing down or cessation of the reaction is due apparently to the formation of a form of ferrous sulphate monohydrate on the surface of the iron. Although, generally speaking, increased dilution of the acid with water results in greater reactivity, certain anomalies were observed in this respect, notably that 89·3% acid has considerably less solvent action than either weaker or stronger acid of 94%, 90·9%, 87·9%, or 85% strength. The solvent effect is in all cases noticeably increased by shaking the containing vessel. G. F. M.

The Critical Points of Self-hardening Steels. P. DEJEAN (*Compt. rend.*, 1919, **169**, 1043—1045).—It has previously been shown (A., 1917, ii, 477) that there is a distinct discontinuity between the formation of perlite or troostite and martensite, the critical point corresponding with the formation of the former being "*A*" and of the latter "*B*." It is now noted from a study of the cooling curves of a nickel–chrome–copper steel, which, starting from different initial temperatures, was cooled from 700° to 100° in about one hundred and fifty minutes, that the formation of martensite apparently occurs in two stages denoted by critical points B_1 and B_2. The point *A* is indicated only when the critical temperature of cooling is 790°. When this temperature rises to 800°, *A* is considerably suppressed and the critical point B_1 appears at about 420°. If the steel is cooled from 850° the second point B_2 occurs at about 230°, and if cooled from still higher temperatures B_1 disappears and the point B_2 exists alone. If only the point *A* is in evidence during cooling the steel is relatively soft, but becomes harder when B_1 predominates and still harder when B_2 appears. It is concluded that for the steel studied the maximum hardness is reached in at least two stages, and that for the same steel there may be several martensitic forms. W. G.

The Formula of Chromium Hydroxide. MIL. Z. JOVITSCHITSCH (*Helv. Chim. Acta*, 1920, **3**, 46—49).—The solubility of chromium hydroxide in ammonia and the preparation from such solutions of complex salts which invariably contain $10H_2O$ (compare

A., 1913, ii, 223) leads the author to assign the formula $Cr_4(OH)_8O_2,10H_2O$ or $Cr_4(OH)_{10}O,9H_2O$ to chromium hydroxide. Stronger evidence in favour of such formulation is found in the absorption of carbon dioxide from the air by chromium hydroxide with the formation of a carbonate, $CO_3,2Cr_2(OH)_6,8H_2O$, to which the formula $\begin{array}{l}Cr_2(OH)_5\cdot O\\Cr_2(OH)_5\cdot O\end{array}\!\!>CO,9H_2O$ or $O<\begin{array}{l}Cr_2(OH)_4\cdot O\\Cr_2(OH)_4\cdot O\end{array}\!\!>CO,10H_2O$ is ascribed (compare A., 1914, ii, 373). H. W.

Chromium Chromate, $CrO_3,Cr_2O_3,7H_2O$. MIL. Z. JOVITSCHITSCH (*Helv. Chim. Acta*, 1920, **3**, 40—46).—When a solution of chromium oxide in nitric acid (compare A., 1912, ii, 261) is evaporated until excess of acid is removed and the residue is dissolved in water and treated with ammonia, a dark brown, almost black product is obtained, analyses of which are in agreement with the formula $Cr_2(OH)_8,H_2O$ or $CrO_3,Cr_2O_3,7H_2O$. The loss of $1H_2O$ over sulphuric acid, of $2H_2O$ at 105°, and of $6H_2O$ at 205° is more readily explained by the former, but the chromium content and particularly the possibility of the preparation of anhydrous chromium chromate from the substance, lead the author to give preference to the latter. The substance is somewhat unstable and loses chromium trioxide when repeatedly washed even with warm water. It forms a very suitable initial material for the preparation of pure chromium hydroxide free from alkali, which is effected by boiling a solution of the substance in concentrated hydrochloric acid with alcohol until reduction is complete and subsequently adding ammonia in excess.

Anhydrous chromium chromate cannot be prepared by heating the hydrated product, since decomposition occurs before the last molecule of water is removed; it may, however, be obtained as a porous, black mass by dissolving chromium oxide in nitric acid, evaporating the solution to dryness, and cautiously heating the residue to 290°. The analytical data agree equally well with those required for the peroxide, CrO_2, but the readiness with which the substance is converted by ammonia, alkali carbonate, or hydroxide or by boiling water into chromium hydroxide and chromate is interpreted in favour of a salt-like constitution. H. W.

Electro-deposition of Nickel. L. D. HAMMOND (*Trans. Amer. Electrochem. Soc.*, 1916, **30**, 103—134).—The best conditions for securing a satisfactory anode corrosion in the electro-deposition have been sought by studying the polarisation pressures and the current efficiency obtained with anodes of cast nickel, electrolytic nickel, and annealed nickel in solutions of nickel sulphate containing measured amounts of boric acid and nickel chloride. The experiments show that although cast nickel anodes corrode fairly well in simple sulphate solutions to which boric acid has been added, the best results are obtained when the purest electrolytic nickel in nickel sulphate solutions containing chloride is used. Nickel chloride is to be preferred to other chlorides, as its addition does

not decrease the concentration of nickel in the electrolyte. It is shown that 6 grams of nickel chloride per litre produce a good anode corrosion, and that the best results are secured by increasing the concentration of nickel chloride to 15 grams per litre. The conditions necessary for the direct electro-deposition of nickel on zinc have been investigated. It is shown that nickel can be directly deposited on zinc from the baths used to deposit nickel on more electro-negative metals if a higher initial current density is employed than is usual when using these baths for their ordinary purposes. An electrolyte consisting of 120 grams of nickel sulphate, 15 grams of nickel chloride, 30 grams of boric acid, and 1000 c.c. of water may be used to deposit nickel on zinc, copper, brass or iron. To deposit on copper a current density varying from a few tenths of an ampere to 3 or 4 amperes may be used, but to deposit on zinc a current density of not less than 3 amperes must be employed. It is suggested that whilst the above-named bath produces good deposits on flat strips of zinc, it will probably give a deposit with black streaks if irregular objects are to be plated. The following bath composition, however, produces perfect deposits on irregular objects: 240 grams of nickel sulphate, 15 grams of nickel chloride, 30 grams of boric acid, 175 grams of sodium citrate, and 1000 c.c. of water. This bath gives good deposits with current densities 0·5—7 amperes per sq. dcm. if pure nickel anodes are used. The two baths named are very rapid in their action. Nickel has been deposited directly on zinc from a $N/2$-solution of hydrochloric acid containing 120 grams of nickel sulphate per litre. Sodium citrate has a beneficial effect on baths for the direct nickeling of zinc, which is not due to a change in the potential of zinc, but to a decrease in the rate of deposition by immersion. Sodium potassium tartrate and sodium malate have a similar action, but they do not permit the use of so high a current density as the citrate bath. The substitution of nickel ammonium sulphate by nickel sulphate in nickeling baths is recommended. To ensure a good deposit of nickel it is essential that the bath should be slightly acid, and it is for this purpose that boric acid is added. The function of the boric acid is therefore to maintain a small but fairly constant concentration of hydrogen ions in the electrolyte.

J. F. S.

Isolation of Molybdenum and working up of Molybdenum Residues. S. Malowan (*Chem. Zeit.*, 1918, **42**, 410).—To recover molybdic acid used as a precipitant in phosphorus determinations, the liquor is precipitated with sodium or calcium phosphate. The yellow precipitate, after being washed and dried, is heated with excess of concentrated sulphuric acid until solution is complete and the acid colourless. The cold liquid is poured into eight to ten times its volume of water, and the molybdenum precipitated with excess of ferrocyanide. The precipitate is collected after three hours, washed with dilute ferrocyanide solution until all the acid is removed, dried, separated from the paper, and ignited at a dark red heat to incipient fusion. The cooled product is leached

twice with hot water, then extracted with ammonia, which dis solves molybdic acid. The colourless solution is filtered, evaporate to dryness, the residue dissolved in a little water and hydroge peroxide, and the solution boiled to oxidise any lower oxides. Th resulting solution of ammonium molybdate is diluted until it ha D^{17} 1·09 (that is, 10 per cent.). W. R. S.

Reversible Reaction of Water on Molybdenum. GEORGE CHAUDRON (*Compt. rend.*, 1920, **170**, 182—185).—A study of th system water vapour–molybdenum–hydrogen–molybdenum dioxid over the temperature range 700—1100°. The values c $K = p_{H_2O}/p_{H_2}$ obtained by the oxidation of the metal or the reduc tion of the oxide agree closely. Plotting log K against $1/T$, th points obtained lie on a straight line within the temperatu interval considered. W. G.

The Violet Compounds of Uranium. J. ALOY and] RODIER (*Bull. Soc. chim.*, 1920, [iv], **27**, 101—105).—The produ tion of violet compounds of uranium as described by Aloy (compa A., 1901, ii, 317) is not an exceptional phenomenon, but quit general, and does not necessarily involve the action of light. It necessary to distinguish between salts of inorganic acids and sal of organic acids. Salts of the first type must be used in exact neutral solution and in the presence of a readily oxidisable su stance. Both violet and ultra-violet rays cause the production violet precipitates, the ultra-violet rays being the more active. T action of light is not always necessary, and it is shown that the violet compounds are obtained whenever a uranous and a uran salt are present together at the requisite temperature in a neutr or feebly acid medium.

In reality, there exist a large number of violet compounds uranium, having an analogous constitution, all of which, by loss their acid radicles, tend to become transformed into the gree hydrated oxide, $U_3O_8,2H_2O$. W. G.

Soluble Metastannic Acid. HANS KREIS (*Schweiz. Che Zeit.*, 1919, 389).—Spongy tin is dissolved in a solution of fer nitrate in nitric acid, D 1·23, and, after the vigorous reaction h subsided, hot water is added. The resulting, slightly opalesce solution contains colloidal metastannic acid, and may be repeated evaporated to dryness, with or without addition of more nitric aci without precipitation of the tin (compare Antony and Mondoll A., 1899, ii, 330). The author considers that the ferric hydroxi formed by dissociation of the ferric nitrate acts as a protecti colloid. A. R. P.

The Question of the Existence of Zirconium Monoxid R. SCHWARZ and H. DEISLER (*Ber.*, 1920, **53**, [*B*], 1. Compare th vol., ii, 42).—A recognition of similar work by Wedekind (A., 191 ii, 225). J. C. W.

Electrolysis of Aqueous Solutions of Vanadium Salts. SIEGFRIED FISCHER, jun. (*Trans. Amer. Electrochem. Soc.*, 1916, **30**, 175—228).—Several hundred experiments are described in tabular form, which have been made with the object of depositing metallic vanadium from aqueous solutions. After a resumé of the literature of the deposition of vanadium, the author describes fifty-five experiments made with Cowper-Coles vanadium electrolyte (1·75 vanadium pentoxide, 2·00 sodium hydroxide, 160·0 water, and after boiling 32·0 hydrochloric acid) (A., 1899, ii, 755). It is found that in no circumstances can metallic vanadium be obtained from this electrolyte. The reduction of the electrolyte is limited in most cases to the vanadyl state, which is blue (V_2O_4). A reduction occurs in practically all the experiments. At temperatures of 90° or above, the reduction may be taken to the lavender colour (V_2O_2). Lead electrodes alone give a reduction to the sesquioxide (V_2O_3), or green state, at temperatures below 90°; above 90° the electrolyte is reduced to the lavender state. Carbon electrodes reduce the electrolyte to the green state. At temperatures below 90° platinum electrodes reduce the electrolyte to the blue vanadyl state only, and the current density has no influence on this. At temperatures above 90° the lavender state is reached only when porous cells are used. The black deposit obtained by Cowper-Coles on platinum electrodes is not a vanadium compound, but platinum hydride. A number of experiments (112) were made with solutions of vanadium pentoxide in sulphuric acid in the presence of various concentrations of aluminium sulphate, magnesium sulphate, ammonium sulphate, hydrofluoric acid, boric acid, or silicic acid, using electrodes of platinum, carbon, lead, and mercury. When platinum electrodes were used a black film was obtained, which contained no vanadium. In no case was metallic vanadium obtained. Solutions of vanadic acid in hydrochloric acid, sulphuric acid, nitric acid, hydrofluoric acid, lactic acid, ethyl hydrogen sulphate, and tartaric acid were electrolysed, as well as a series of solutions of vanadic oxide in alkali hydroxide, but in no case could metallic vanadium be obtained. The reason for the failure to obtain metallic vanadium is the very large heat of formation of vanadium salts. Thus the oxide V_2O_5 has a heat of formation 441000 cal.; V_2O_3, 353200 cal.; VO, 104300 cal. J. F. S.

Formation and Nature of Black Antimony Trisulphide. FERRUCCIO DE BACHO (*Annali Chim. Appl.*, 1919, **12**, 143—152).—On heating red antimony trisulphide in carbon dioxide, there is no material difference in the loss of weight at temperatures from 150° to 300°, the change to the black modification taking place at 212°, whilst in a current of hydrogen sulphide the change occurs at 207°. By adding ammonium chloride to the red sulphide, the temperature of the change in carbon dioxide is lowered (for example, to 170°), whilst the presence of antimony chloride reduces the temperature still further. Thus in the case of a mixture of equal parts of antimony trisulphide and trichloride, the black

coloration appeared at 125°. Metallic silver also has a favourable influence on the transformation. The action of ammonium chloride in boiling solution also promotes the formation of the black sulphide to an extent depending on the concentration of the solution, whilst the rapidity of the transformation stands in relationship to the degree of hydrolysis of the ammonium chloride, and consequent acidity of the solution. The presence of antimony trichloride facilitates this conversion, which is accelerated by the presence of hydrochloric acid, antimony trisulphide, and potassium nitrate at high concentrations. Concentrated solutions of electrolytes, such as sodium chloride, ammonium sulphate, or potassium nitrate alone have no effect on the transformation, which is therefore not merely the result of molecular condensation. The conversion always takes place when the conditions permit of immediate contact between the red antimony trisulphide and antimony trichloride, whether added as such or formed in the solution. It is probable that the following reaction takes place: $2Sb_2S_3 + 2SbCl_3 \longrightarrow 6Sb + 3S_2Cl_2$. It is also probable that the trace of free antimony thus formed, or that produced by dissociation of the red trisulphide when heated, forms in the colloidal condition a solid solution with the antimony trisulphide. This decomposition, which occurs in the process of drying in analytical work, is too small to be detected gravimetrically. On heating the red trisulphide, there is a gradual increase in the specific gravity, but the conversion into the black modification is not indicated by any sudden rise in the specific gravity.

C. A. M.

The Action of Aqua Regia on Gold-Silver Alloys in the Presence of Ammonium Salts. WILLIAM BRANCH POLLARD (T., 1920, **117**, 99—103).

Mineralogical Chemistry.

Colloid Colour Substances in Minerals. C. DOELTER (*Kolloid Zeitsch.*, 1920, **26**, 23—27).—A theoretical paper in which it is shown that the colours of many minerals are due to small quantities of impurities, which may be the same in differently coloured minerals. The nature of the colour depends on the size of the particles of the pigment. Change in the colour effected by heating or by the action of radium rays is due to a change in the dimensions of the particles.

J. F. S.

A Markedly Ceritic Fluoapatite from Latium. I. BELLUCCI and L. GRASSI (*Gazzetta*, 1919, **49**, ii, 232—246).—A nodule included in the building stone known as "peperino," occurring in a cave in the Ariccia district, is found to consist principally of olivine and biotite, together with numerous small, shining, crystalline aggregates having a radiating, fibrous structure and a pale emerald-green colour. This green mineral, D 3·23—3·29,

n 1·63—1·65, is a fluoapatite containing comparatively large proportions of rare earths; analysis gave:

CaO.	Rare earth oxides.	FeO.	P_2O_5.	SO_3.	F.	Total.
50·86	5·24	1·92	35·5	2·59	3·37	99·48

The rare earths present are ceritic and not yttric in character, the presence of cerium, didymium, and lanthanum being demonstrated.

A summary is given of the literature dealing with apatites containing rare earths. In the apatite of Narsarsuk, Flink (A., 1900, ii, 410) found 3·36% of yttric oxides and 1·52% of ceritic oxides.

T. H. P.

The Origin of the Beds of Sodium Carbonate in Peru. EMM. POZZI-ESCOT (*Bull. Soc. chim.*, 1919, [iv], **25**, 614—617).—It is suggested that the sodium sulphate of the soil dissolves in the water which gradually collects in natural depressions, forming salt marshes, with an abundance of vegetation suited to the conditions. The sulphate in contact with the plants and algæ becomes reduced to sulphide, which is then in its turn decomposed by carbon dioxide, either atmospheric or that resulting from local vegetative combustion, with the resulting formation of sodium carbonate or sodium hydrogen carbonate. The industrial possibilities of these deposits are discussed.

W. G.

Mineralogy of Sweden. GUST. FLINK (*Arkiv Kemi Min. Geol.*, 1917, **6**, No. 21, 1—149).—In Part IV of his "Mineralogy of Sweden," the author gives detailed descriptions of forty-five

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	PbO.	GlO.
I	16·61	—	—	—	77·63	—
II	16·50	—	—	—	77·70	—
III	17·74	—	—	—	66·53	—
IV	17·21	—	—	—	70·14	—
V	39·84	—	—	0·15	—	16·53
VI	40·00	—	—	trace	—	11·49
VII	37·53	23·79	7·73	3·85	—	—
VIII	45·53	23·07	1·93	—	—	—
IX	43·54	22·62	1·79	—	—	—
X	43·40	23·05	1·27	—	—	—

	MnO.	CaO.	MgO.	H_2O.	Total.	Sp. gr.
I	0·35	1·75	0·41	0·40	99·95*	6·53
II	2·83	0·52	0·10	0·08	99·82†	6·706
III	2·88	10·42	0·45	0·60	99·11‡	5·576
IV	2·78	7·31	0·95	—	98·39§	—
V	26·82	15·67	0·55	0·54	100·10	3·404
VI	7·05	37·82	0·94	2·48	99·93‖	3·16
VII	0·48	21·97	0·34	3·14	99·63**	3·189
VIII	—	25·48	—	4·48	100·49	—
IX	—	26·56	—	4·81	99·32	2·914
X	trace	26·49	0·40	4·89	99·50	2·906

* Including Fe 0·10, Cl trace.
† Including ZnO 0·90, K_2O 0·09, Na_2O 0·40, SO_3 0·63, Cl 0·12.
‡ Including Na_2O 0·06, K_2O 0·17, CO_2 0·26.
§ Including Cl 0·10.
‖ Including F 0·15.
** Including TiO_2 0·11, K_2O 0·24, Na_2O 0·45.

species belonging to the silicate group. Analyses are given of the following: I and II, barysilite of different types from Jakobsberg; formula, $Pb_3Si_2O_7$. Ganomalite, III, from Jakobsberg, IV from Långban. V, trimerite from Jakobsberg; formula, $Gl_2SiO_4,(Mn,Ca)_2SiO_4$. VI, harstigite from Harstig mine; formula, $Gl_2Ca_3Si_3O_{11}$. VII, epidote from Nols felspar quarry, Göta. Prehnite, VIII from Uppsala district, IX from Hästberg estate, near Falun, X from Sjösa iron mine, near Svärta.

L. J. S.

Presence of Lithium in the Salts of Vesuvian Fumaroles. L. DE LUISE (*Gazzetta*, 1919, **49**, ii, 328—329).—The salts from the fumaroles of the crater of Vesuvius have the composition: potassium chloride, 20·521%; sodium chloride, 79·458%; iron and aluminium, traces. Sometimes lithium is present in small proportion, and in one instance 180 grams of the mixed chlorides were found to contain lithium chloride corresponding with 0·07 gram of lithium sulphate.

T. H. P.

Analytical Chemistry.

Qualitative Analysis in the Presence of Phosphoric Acid. HEINRICH REMY (*Zeitsch. anal. Chem.*, 1919, **58**, 385—392).—The following procedure is recommended for the qualitative analysis of a solution containing various metals, etc., and phosphoric acid. Heavy metals are first separated by means of hydrogen sulphide; the filtrate from the sulphide precipitate is boiled to expel hydrogen sulphide, filtered, heated with the addition of a small quantity of nitric acid, then nearly neutralised with ammonium carbonate, treated with an equal volume of concentrated ammonia, and an excess of ammonium phosphate is added. Aluminium, chromium, iron, calcium, strontium, barium, manganese, and magnesium are precipitated, whilst zinc, nickel, cobalt, and alkali metals remain in solution. The precipitate is dissolved in warm dilute hydrochloric acid, potassium sulphate solution is added, and the precipitated alkali earth sulphates are collected on a filter and separated and identified in the usual way. The filtrate from the sulphates is boiled with the addition of sodium acetate and ammonium chloride; iron, chromium, manganese, and aluminium are precipitated, whilst magnesium and a small quantity of calcium remain in solution. The precipitate is dissolved in hydrochloric acid, boiled, nearly neutralised with sodium carbonate, and then poured into a mixture of hydrogen peroxide and 20% sodium hydroxide solution. Iron and manganese are precipitated, whilst chromium and aluminium are converted into soluble chromate and aluminate respectively. The filtrate from the first phosphate precipitate, and

containing the zinc, etc., is heated, treated with ammonium sulphide, the precipitate is collected (the filtrate from this precipitate contains the alkali metals), and the zinc sulphide is dissolved in dilute hydrochloric acid, in which nickel sulphide and cobalt sulphide are insoluble. The hydrochloric acid solution is then rendered strongly alkaline with sodium hydroxide, heated, diluted, and filtered; zinc is precipitated from the filtrate as sulphide after the addition of acetic acid. Nickel and cobalt are separated and identified in the usual way. W. P. S.

Method of Stating Analytical Results. A. THIEL (*Chem. Zeit.*, 1920, **44**, 81—82).—*A discussion advocating the use of* equivalent units in expressing the results of analysis. W. P. S.

Influence of Temperature on the Strength of Standard Solutions in Quantitative Analysis. YUKICHI OSAKA (*J. Tokyo Chem. Soc.*, 1919, **40**, 424—449).—The tables previously published (*ibid.*, 1911, **32**, 450) showing the changes in the concentration of *standard solutions at different temperatures*, taking 15° as the standard temperature, have been extended for temperatures from 5° to 30°, each being compared with three standards, at 15°, 20°, and 25°. Nineteen tables are given for *N*- and *N*/10-oxalic acid, *N*-hydrochloric, nitric, and sulphuric acids, *N*- and *N*/10-sodium carbonate, *N*/10-sodium hydroxide, *N*/10- and *N*/100-sodium chloride, *N*/10- and *N*/100-silver nitrate, *N*/10- and *N*/100-potassium permanganate, *N*/10-ammonium thiocyanate, and water. The change in the concentration of the solution and in the volume of the flask produced at different temperatures is recorded. The results are summarised in the following table:

Standard temp.:	15°.		20°.		25°.	
Solution temp.:	5°.	30°.	5°.	30°.	5°.	30°.
NaOH (*N*)	1·00245	0·99508	1·00393	0·99655	1·00559	0·99819
Na_2CO_3 (*N*)	1·00230	0·99521	1·00374	0·99664	1·00534	0·99820
HNO_3 (*N*)	1·00227	0·99516	1·00371	0·99658	1·00534	0·99822
H_2SO_4 (*N*)	1·00231	0·99516	1·00365	0·99659	1·00526	0·99818
$H_2C_2O_4$ (*N*)	1·00160	0·99580	1·00279	0·99698	1·00422	0·99840
HCl (*N*)	1·00153	0·99608	1·00264	0·99718	1·00395	0·99849
NaCl (0·1*N*)	1·00108	0·99642	1·00201	0·99735	1·00321	0·99854
$AgNO_3$ (0·1*N*)	1·00105	0·99640	1·00202	0·99737	1·00321	0·99856
NH_4CNS (0·1*N*)	1·00104	0·99639	1·00199	0·99734	1·00322	0·99856
$KMnO_4$ (0·1*N*)	1·00096	0·99643	1·00193	0·99737	1·00312	0·99856
Na_2CO_3 (0·1*N*)	1·00095	0·99675	1·00177	0·99757	1·00287	0·99866
$H_2C_2O_4$ (0·1*N*)	1·00078	0·99674	1·00161	0·99757	1·00270	0·99866
NaCl (0·01*N*)	1·00089	0·99649	1·00178	0·99738	1·00295	0·99853
$AgNO_3$ (0·01*N*)	1·00089	0·99655	1·00177	0·99743	1·00294	0·99858
$KMnO_4$ (0·01*N*)	1·00087	0·99653	1·00181	0·99745	1·00294	0·99858
H_2O	1·00083	0·99661	1·00174	0·99751	1·00288	0·99864

The average from all *equinormal solutions is given* in the final table for each temperature from 5° to 30° against three standard temperatures. This table could be used for any *N*-solution, within error of 5 in 10,000. Another table is given which could be applied for any solution less than 0·1*N* within error of 5 in 10,000. It is

pointed out that maximal errors for two solutions of equal strength made at two extreme temperatures (5° and 30°) is 7:1000 for N and 5:1000 for solutions less than $0 \cdot 1N$.

CHEMICAL ABSTRACTS.

The Effect of a Change in Temperature on the Colour Changes of Methyl-orange, and on the Accuracy of Titrations. HENRY THOMAS TIZARD and JOHN REGINALD HARVEY WHISTON (T., 1920, **117**, 150—156).

Indicator Papers. D. J. DE JONG (*Pharm. Weekblad*, 1919, **56**, 465—467).—An extension and amplification of previous communications (*ibid.*, 179, 238, 328, 404, 405). If a drop of acid is placed on ordinary filter paper and tested with methyl-orange, a weak reaction will be indicated in a ring surrounding the drop, and beyond this will exist a neutral "water ring." If the paper is previously treated with hydrogen chloride, washed, and dried, it becomes saturated with hydrogen ions, and further absorption of these from the drop will be prevented. A stronger coloration will thus result, and will be produced in the whole moistened portion. Addition of acid to methylene-blue similarly increases its sensitiveness.

W. J. W.

Use of the Electrometer for Titrations. J. PINKHOFF (*Pharm. Weekblad*, 1919, **56**, 1218—1234).—The author gives a description of the apparatus and mode of operation in carrying out titrations by the potential method. A difference of potential of 1 millivolt should be detected by a suitable electrometer. The scope of the method and its special applications are discussed at some length.

W. J. W.

Use of Arsenious Anhydride in Namias' Method of Volumetric Analysis. FERRUCCIO DE BACHO (*Annali Chim. Appl.*, 1919, **12**, 136—142).—In Namias's method (A., 1892, 1374) any given oxidising agent is treated with an excess of arsenious anhydride in the presence of ammonium acetate, and the boiling liquid titrated with iodine solution after the addition of acetic acid. Critical experiments have shown that this method is untrustworthy. No blue coloration is given by starch paste with iodine at 60—70°, and it is therefore useless to employ it as an indicator in a boiling solution. The presence of ammonium chloride formed from the ammonium acetate when the solution contained hydrochloric acid also influences the results. Equilibrium between the reacting substances is then only very slowly attained. Contrary to the assertion of Namias, the reaction between arsenious anhydride and chromic acid is only complete after prolonged action, and the results obtained are invariably too high and not concordant.

C. A. M.

New Volumetric Reduction Method with Arsenious Anhydride. FERRUCCIO DE BACHO (*Annali Chim. Appl.*, 1919, **12**, 153—174).—An oxidising agent is treated with excess of arsenious

acid solution in the presence of hydrochloric acid, and the solution subsequently titrated with standard potassium bromate solution, methyl-orange being used as indicator. To prevent loss through volatilisation of arsenic chloride the proportion of hydrochloric acid must not exceed 12·8%, a distinct loss occurring when it reaches 15%. In many cases the reduction is complete at the ordinary temperature, but as a rule it is preferable to boil the liquid beneath a reflux condenser. The method gives good results in the analysis of permanganates, in the estimation of manganese dioxide in pyrolusite, and the analysis of chlorates and chromates, including lead chromate. In the case of mixtures of hypochlorites and chlorates the hydrochloric acid is reduced to 5% to retard the action of the chlorate during the estimation of the hypochlorites. The acid is then increased to 12% and the reduction effected at boiling point, when both chlorates and hypochlorites react, and the amount of the former is found by difference. [See, also, *J. Soc. Chem. Ind.*, 1920, March.] C. A. M.

Improved Electro-analysis Apparatus. J. L. Jones (*Trans. Amer. Electrochem. Soc.*, 1917, **32**, 329—334).—A description of a six- and a ten-unit electrically stirred electrolytic apparatus for the quantitative analysis of non-ferrous alloys. The electrodes and beakers are fixed; stirring is effected by revolving tungsten rods. Each electrolysis receives a separate current which may be varied between 0·5 and 6·0 amps. A switch and push-button before each unit enable the current and *E.M.F.* to be read at any moment. J. F. S.

Use of Lead as a Substitute for Platinum in Analysis. Carl Hütter (*Zeitsch. angew. Chem.*, 1919, **32**, 380).—Platinum basins may be replaced by lead basins for certain quantitative estimations. Thus in the case of chrome iron ore the mineral may be heated with concentrated sulphuric acid in a lead basin on the water-bath, and any lead sulphate formed removed without interfering with the subsequent analysis. The method is suitable for the estimation of silicon, aluminium, potassium, and sodium, for which silica or silver basins cannot be used. Any alteration in the stage of oxidation is prevented by introducing a current of carbon dioxide through a porcelain tube inserted into a hole in the middle of the lead cover of the basin. C. A. M.

Catalytic Reduction of Organic Halogen Compounds. M. Busch (*Zeitsch. angew. Chem.*, 1918, **31**, 232).—In the catalytic reduction of organic halogen compounds by means of palladium, hydrazine may be substituted with advantage for a current of purified hydrogen. 0·2 Gram of the organic compound is dissolved in 40—50 c.c. of alcohol; 2 grams of palladinised calcium carbonate, or barium sulphate, 2·5 c.c. of 50% potassium hydroxide, and 10 drops of hydrazine hydrate are added. The liquid is boiled under reflux for thirty minutes, after which the bulk of the alcohol

is expelled on the water-bath. The catalyst is filtered off, and the halogen determined in the filtrate after acidification with nitric acid. W. R. S.

Estimation of Organic Chlorine or Bromine by the Chromic Acid Method. P. W. ROBERTSON (*Chem. News*, 1920, **120**, 54).—To overcome minor difficulties encountered in the chromic acid method of estimating organic chlorine or bromine (T., 1915, **107**, 902), the following modifications are suggested. A freshly prepared cold solution of sodium peroxide is used as absorbing medium instead of sodium hydroxide solution containing hydrogen peroxide. The chromic anhydride may be replaced by halogen-free potassium dichromate, and $N/20$-solutions of silver nitrate and ammonium thiocyanate are recommended instead of $N/10$-solutions. Finally, in the case of compounds, particularly liquids, which react explosively with the oxidising mixture, the best procedure is to cover the substance with a large amount of powdered dichromate and run the previously cooled sulphuric acid very rapidly into the reaction vessel through a wide funnel by means of a suction pump connected with the absorption tube. The reaction vessel is cooled in ice until the initial violence of the oxidation has moderated. G. F. M.

Iodometric Estimation of Chloric Acid. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 460—465).—The direct iodometric estimation of chlorate in a strongly acid medium gives high results owing to oxidation of hydrogen iodide by atmospheric oxygen. Rupp's method (A., 1918, ii, 125) is satisfactory. It is sufficient, however, to use hydrochloric acid to the extent of one and a-half times the volume of the chlorate solution, and only 100 c.c. of potassium iodide need be added. By using ferrous sulphate, still smaller quantities of reagents may be employed. The chlorate solution is boiled with 10 c.c. of $4N$-hydrochloric acid and ferrous sulphate; 1 gram of potassium iodide is added at 50°, and the solution then titrated with slight heating towards the end. W. J. W.

Estimation of Iodide. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 1029—1035).—Estimations were made by several known methods with the same preparation of potassium iodide ($0·098N$) in each case. Winkler's method (*Zeitsch. anal. Chem.*, 1914, **53**, 20) gives good results only in absence of bromide. The presence of bromide in small quantities does not affect the results in the case of those methods in which hydrogen iodide is oxidised to iodine and the latter estimated, for example, Volhard's, Vincent's (A., 1900, ii, 166), and Richard's (*Pharm. Weekblad*, 1903, **40**, 157). In the last-mentioned method, it is advisable to let the solution remain for two to three minutes after addition of the tartaric acid. Iodide may be estimated in presence of bromide by adding benzoic acid and potassium iodate, boiling until the iodine has disappeared, then adding potassium iodide and sulphuric acid, and titrating back with thiosulphate. W. J. W.

Estimation of Oxygen with Cuprammonium Compounds. W. HAEHNEL and M. MUGDAN (*Zeitsch. angew. Chem.*, 1920, **33**, 35).—In the preparation of ammoniacal copper solution for the absorption of oxygen, the usual ammonium carbonate solution employed may, with advantage, be replaced by saturated ammonium chloride solution. The rate of absorption of oxygen is not affected, but the residual gas is free from carbon dioxide derived from the ammoniacal copper solution. W. P. S.

The Volumetric Estimation of Sulphates by Oxidation of Benzidine Sulphate with Potassium Permanganate. P. L. HIBBARD (*Soil Sci.*, 1919, **8**, 61—65).—A modification of the method of Raiziss and Dubin (compare A., 1914, ii, 671), full details being given. It is shown that both temperature and volume are important factors, which should be kept constant. The solution for the precipitation of benzidine sulphate should be free from organic matter, iron, the heavy metals, nitrates, and phosphates, and should contain between 0·5 and 4·0 mg. of SO_4''. It is advisable to use an excess of standard permanganate solution, the oxidation flask being heated in a boiling-water bath for ten minutes. At the end of this time, a slight excess of standard oxalic acid solution is run in, and this is then titrated back with the permanganate solution. W. G.

Estimation of the Non-protein Nitrogen in Blood. B. ALBERT (*Biochem. Zeitsch.*, 1918, **92**, 397—412).—A modification of the micro-method for estimating the non-protein nitrogen in blood. The blood or serum is freed from its protein by the addition of colloidal iron and 10% potassium sulphate. The filtrate is oxidised with "micro-sulphuric acid," consisting of 15 grams of nitrogen-free potassium sulphate, 5 grams of pure copper sulphate, 100 c.c. of distilled water, and 400 c.c. of pure concentrated sulphuric acid. The distillation is carried out in an apparatus described by the author. The distilled ammonia is received in *N*/200-sulphuric acid and estimated iodometrically. S. S. Z.

Estimation of Urea Nitrogen in Blood (and Urine). B. ALBERT (*Biochem. Zeitsch.*, 1919, **93**, 82—89).—The Lesser-Siebeck micro-method for the estimation of urea nitrogen is considered a very suitable one. Some modifications are recommended. S. S. Z.

Estimation of Small Quantities of Arsenic. W. VAN RIJN (*Pharm. Weekblad*, 1919, **56**, 1072—1083).—Various methods of estimation of small quantities of arsenic, as in urine, have been investigated. Separation of the arsenic from the material under test is accurately effected by several methods, as follows: (*a*) Treatment with potassium chlorate and hydrochloric acid (Fresenius and Babo); (*b*) absorption by ferric hydroxide (Lockemann and Paucke, A., 1911, ii, 720); (*c*) acidification of the sample with

sulphuric acid, addition of solution of bromine in potassium bromide, then ammonia and magnesia mixture; (*d*) treatment with ammonia and magnesia mixture, and addition of sodium phosphate (Berntrop). Bloemendaal's apparatus was used for obtaining the mirror; final estimation of this by comparison with a standard mirror was not accurate, and the titration method (Berntrop, A., 1906, ii, 706) was used. Quantities as small as 1 mg. of arsenic per litre were estimated. The estimations were also carried out with wallpapers, paint, and blind materials. W. J. W.

Precision Method for the Estimation of Gases in Metals. H. M. Ryder (*Trans. Amer. Electrochem. Soc.*, 1918, **33**, 197—204).—The metal to be investigated is mounted as a thin ribbon or filament in an electric light bulb, which is connected to a Toepler pump and exhausted. The temperature of the filament is then raised by an electric current, and the pump set working, so that the gases are continuously removed. The temperature is raised in steps of 50° up to the melting point, and the gases evolved at each temperature are measured and analysed. The bulb is water-cooled to prevent the evolution of gases by the glass on heating. Silicon steel was found to give off large volumes of gas at 730°. In the analysis, the water vapour and carbon dioxide are frozen out by means of liquid air, and the remaining gases removed. The carbon dioxide is then removed by substituting carbon dioxide snow for the liquid air. The volume of carbon dioxide is measured by reading the pressure existing in the apparatus by means of a MacLeod gauge. It is then pumped out, and the water vapour released into the vessel by removing the refrigerant. The pressure due to this is read by means of a mercury U-tube manometer with optical lever attachment. Oxygen is added to the residual gases, and the hydrogen, methane and carbon monoxide are burnt to carbon dioxide and water, which are estimated as before. Carbon monoxide is added to the residual gases, and serves, after combustion, to estimate the excess of oxygen and any which may have been there originally. Nitrogen is estimated by difference. J. F. S.

New Absorption Apparatus for Elementary Analysis. Fritz Friedrichs (*Zeitsch. angew. Chem.*, 1919, **32**, 388).—A compact form of absorption apparatus is described in which the carbon dioxide is absorbed by means of potassium hydroxide solution in a belical tube, which is fixed within the bend of a U-tube. The latter is charged with calcium chloride instead of soda-lime. The use of calcium chloride as a drying agent is preferable to that of sulphuric acid when it is a question of equilibrium being attained. The binary system $CaCl_2$–H_2O, in which the phases $CaCl_2$, $CaCl_2,2H_2O$, H_2O occur, is univariant, and the tension there- mæe depends on the temperature, but not on the concentration, and ;eas the system H_2SO_4–H_2O, in which only two phases, H_2SO_4, adding ᵛe formed, is bivariant, and its tension depends on the con- with thion as well as on the temperature. The use of both drying

agents, as hitherto, is unsuitable, since the tension of sulphuric acid is lower than that of $CaCl_2,2H_2O$. The gas must therefore be moistened, not dried, in the calcium chloride tube following the sulphuric acid vessel, or the results for hydrogen will be too low; under these conditions, calcium chloride dihydrate must be used instead of anhydrous calcium chloride. It is therefore advisable to discard the sulphuric acid and replace it by 50% potassium hydroxide solution and calcium chloride. C. A. M.

Estimation of Combustible Matter in Silicate and Carbonate Rocks. A. C. Fieldner, W. A. Selvig, and G. B. Taylor (*U.S. Bureau of Mines*, 1919, Tech. Paper 212).—The method described is a modification of that devised by Lissner (*Chem. Zeit.*, 1910, **34**, 37—38), involving digestion of the silicate material with hydrofluoric and hydrochloric acids, and combustion of the insoluble residue. Carbonate rocks are treated with dilute hydrochloric acid to remove calcium carbonate, *etc.*, and the process is applied to the insoluble residue. [See, further, *J. Soc. Chem. Ind.*, 1920, 155A.] W. E. F. P.

The Estimation of Calcium and Magnesium in Different Saline Media. E. Canals (*Bull. Soc. chim.*, 1919, [iv], **25**, 655—658. Compare A., 1919, ii, 34, 477).—For the volumetric estimation of small quantities of magnesium it is recommended that the magnesium should first be precipitated as magnesium ammonium phosphate, and then one of two methods adopted.

(1) The precipitate is washed centrifugally with dilute ammonium hydroxide and then dissolved in just sufficient 5% hydrochloric acid, the phosphoric acid in the solution being estimated by titration with an uranium solution (1 c.c. = 0·5 mg. P_2O_5), using cochineal as an indicator. The results are accurate to 0·2 gram of magnesium.

(2) The precipitate is washed with a saturated aqueous solution of sodium phosphate, and then dissolved in hydrochloric acid, the ammonia present being estimated colorimetrically by means of Nessler's reagent. The results are accurate to 0·01 gram of magnesium. W. G.

Spectroscopic Estimation of Small Amounts of Lead in Copper. C. W. Hill and G. P. Luckey (*Trans. Amer. Electrochem. Soc.*, 1917, **32**, 335—343).—A method is described for the rapid estimation of small quantities of lead in copper. A known weight (0·1—1·0 gram) of the sample in the form of a shot is placed in a small cavity in the lower positive graphite electrode of a carbon arc, and a fixed or rotating negative electrode used above. The arc is struck, the light focussed on to the slit of a grating spectroscope, and the time required for the complete disappearance of the bright lead line (405·8 $\mu\mu$) from the spectrum, or for its reduction to a definite feeble intensity, is measured by means of a stop-watch. With careful adjustment of the arc, the times vary

regularly with the amount of copper used and with its percentage of lead. Thus 0·2 gram of copper containing 0·004% of lead reqnired 14 secs., whilst 1·0 gram of copper containing 0·038% of lead required 227 secs. A series of experiments made with 0·4 gram samples show that the analyses are sufficiently accurate for use in a copper refinery. J. F. S.

Estimation of Mercury. H. B. Gordon (*Analyst*, 1920, **45**, 41—46).—For the estimation of small quantities of mercury, a coil of copper gauze is suspended in the solution, which has previously received the addition of a small amount of hydrochloric acid and of copper sulphate; the gauze is kept in motion by a motor, and, after a suitable time, is removed from the solution, washed, dried, and weighed. It is then heated in a current of hydrogen, cooled in the same gas, and re-weighed; the loss in weight is due to the volatilisation of the deposited mercury. The volatilised mercury may be collected in a constricted portion of the heating tube and identified by the iodine test. As little as 0·1 mg. of mercury may be detected by the method. Nitrates do not interfere, but antimony, arsenic, bismuth, and silver should not be present, as they are liable to cause error unless the copper gauze is heated at such a temperature that the mercury alone volatilises. [See, further, *J. Soc. Chem. Ind.*, 1920, March.] W. P. S.

Detection and Estimation of Very Small Quantities of Chromium in Minerals and Ores containing Silicates and Carbonates. O. Hackl (*Chem. Zeit.*, 1920, **44**, 63).—One gram of the mineral is fused with eight times its weight of a mixture of sodium carbonate and potassium carbonate, the fused mass is treated with water, a drop of alcohol is added, the mixture heated to reduce and precipitate any manganese compounds present, and the solution is filtered. The filtrate is evaporated, but not so far that alkali salts crystallise out, again filtered, and diluted to a definite volume, which should be from 20 to 50 c.c., according to the quantity of chromium present. The chromium is then estimated colorimetrically, using as a standard a potassium chromate solution containing 0·0511 gram of the salt and a small quantity of sodium carbonate per 200 c.c.; each c.c. of this solution is equivalent to 0·1 mg. of Cr_2O_3. W. P. S.

A Very Sensitive Reagent for Cobalt. I. Bellucci (*Gazzetta*, 1919, **49**, ii, 294—298).—One mg. of cobalt in solution may be detected colorimetrically in 1—2 litres of water by means of α-nitroso-β-naphthol, and in about 17 litres of water by means of β-nitroso-α-naphthol (compare Atack, A., 1915, ii, 652; Jones, A., 1918, ii, 410; Bellucci and Chiucini, this vol., ii, 54). One mg. of nickel in 4—5 litres of water may be detected by means of dimethylglyoxime. T. H. P.

The Theory of Colour Lakes. C. Brenner (*Helv. Chim. Acta*, 1920, **3**, 90—103).—The author has endeavoured to base

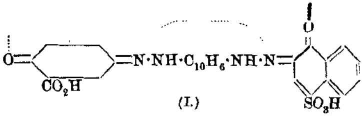
methods for the detection and estimation of minimal amounts of cobalt and copper on the colorations which the metallic ions give with nitrosonaphthols. α-Nitroso-β-naphthol is found to be unsuitable for this purpose in aqueous solution, since the lake is too easily precipitated, whilst chloroform or carbon disulphide solutions (in which cobalt "nitrosite" is readily soluble) are only adapted to the detection, but not to the estimation, of cobalt. On the other hand, the solubility of the lake in water can be sufficiently increased by introducing one or more sulphonic groups into the naphthol molecule. The colour of the lake depends on the number and position of the hydroxy- and sulphonic groups; the yellowest shade is given by the nitroso-derivative of "R"-acid, the deepest red with nitroso-1-naphthol-5-sulphonic acid, and the darkest shade with *nitroso-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid* (chromotropic acid). In ammoniacal solution, the latter gives a lake when metal and acid are in the proportion of 1 atom to 2 molecules, whilst in sodium hydroxide solution the requisite proportion is 1 : 6; attempts to base a colorimetric process for estimating cobalt on these data were unsuccessful, the results being 10—40% high. On the other hand, the acid can be used for the micro-titration of cobalt, since the yellow, ammoniacal solution of nitrosochromotropic acid yields an immediate intense blue coloration with the cobalt ion, in the formation of which 2 molecules of the acid react with an atom of cobalt; when the cobalt ions have been completely converted into this compound, further addition of the acid causes a change in shade from blue to red. Test analyses show the method to be fairly accurate, but it cannot be used for cobalt in the presence of nickel, although the latter alone may also be estimated by the reagent. The micro-titration of copper can be effected similarly, but a larger excess of the reagent is required to give a definite end-point.

Other substances with properties similar to those of nitrosochromotropic acid are found among azo-dyes which are used with metallic mordants, and among those which in dyeing are subjected to after-chroming. Thus, Diamond Black F gives a deep blue solution in aqueous alkali, which yields differently coloured lakes with ammoniacal solutions of the most various metals; when the metallic ion is completely united with the dye, addition of a further quantity of the latter causes a change in shade towards blue. The possible utility of the method is illustrated at the instance of copper.

The possibilities of the formation of differently coloured complex compounds have been investigated for twenty different metals and sixteen dyes; such compounds appear to be formed most frequently with magnesium, the alkaline earth metals, and those of the iron group. It is interesting to note that chromium, which is so largely used in mordanting, is allied in this respect with the least reactive metals of the nitrogen family. The capability of the dye to form differently coloured complex compounds which are soluble in ammonia appears to depend on the presence of a hydroxyl group

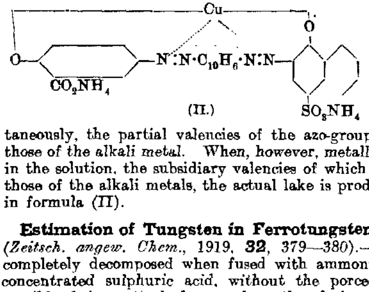
in the *ortho*- or *para*-position to the azo-group, and, as a result of extensive experiments with a number of dyes, it is possible to give methods for the microchemical estimation of copper, silver, magnesium, zinc, cadmium, calcium, strontium, barium, iron, nickel, and cobalt.

The constitution of the lakes and the colour changes involved in the titrations are discussed with particular reference to Diamond



(I.)

Black. In *acid solution*, the *quinonoid formula* (I) is ascribed to the dye in which two strong partial valencies are associated with the oxygen groups, whilst the other partial valencies of the azo-groups satisfy each other. The former valencies are satisfied by the alkali metal in an alkaline solution, and the dye changes its quinonoid for a benz*enoid structure*, whilst, simultaneously, the partial valencies of the azo-groups are satisfied by those of the *alkali metal*. When, however, *metallic ions are present* in the solution, the subsidiary valencies of which are stronger than those of the alkali metals, the actual lake is produced, as indicated in formula (II).



(II.)

H. W.

Estimation of Tungsten in Ferrotungsten. LUDWIG LÖWY (*Zeitsch. angew. Chem.*, 1919, **32**, 379—380).—*Ferrotungsten is* completely decomposed when fused with ammonium sulphate and concentrated sulphuric acid, without the porcelain or platinum crucible being attacked, as when the fusion is effected with potassium hydrogen sulphate. The fused mass is dissolved in water, the solution treated with a little nitric acid, and then boiled with dilute (1 : 5) hydrochloric acid. The precipitated tungstic acid is separated and washed with dilute hydrochloric acid, the filtrate freed from iron by precipitation with ammonia, then acidified, and evaporated to dryness, the residue boiled with dilute hydrochloric acid, and the fresh precipitate of tungstic acid separated. For very accurate analyses, a third precipitation may be made. The united precipitates are ignited until constant in weight, evaporated with hydrofluoric acid, and again ignited and weighed. Any remaining iron may be separated by fusing the residue with sodium carbonate, extracting the mass with water, and weighing the residue of ferric oxide. [See, further, *J. Soc. Chem. Ind.*, 1920, 158A.]

C. A. M.

Estimation of Uranium and its Separation from Other Rare Elements. C. A. Pierlé (*J. Ind. Eng. Chem.*, 1920, **12**, 60—63).—It is shown that good results may be obtained by precipitating uranium with ammonium hydroxide, washing the precipitate with ammonium nitrate solution, and igniting it. Precipitation as uranyl ammonium phosphate by means of ammonium dihydrogen phosphate is also trustworthy, but has the drawback that the ignited uranyl pyrophosphate rapidly absorbs moisture. Precipitation as uranium sulphide and subsequent ignition invariably gives too high results, owing to part of the sulphur being oxidised to sulphate during the ignition. Volumetric estimation of uranium by means of potassium permanganate is inaccurate, owing to over-reduction taking place, and it is not possible to eliminate this or to continue the rednction to a definite point below the uranous condition. A method of separating uranium from vanadium, molybdenum, and tungsten has been based on Peligot's observation (*Ann. Chim. Phys.*, 1842, [iii], **5**, 1) that uranyl nitrate is readily soluble in ether. The solution is evaporated to dryness, and the residue of uranyl nitrate, etc., is extracted with ether, in which vanadium pentoxide, molybdenum trioxide, and tungstic trioxide are insoluble. The dry residue should be moistened with nitric acid immediately before the extraction, and shortly after the process has begun, to reconvert into nitrate the partly decomposed uranyl nitrate. Another method of separating uranium from vanadium has been based on the fact that uranyl nitrate is readily soluble, whereas vanadium pentoxide is insoluble in acetic acid of 95% strength or above to which nitric acid has been added in the proportion of 1 : 20. The solution of uranyl nitrate and sodium metavanadate is evaporated to dryness with nitric acid, and the uranium extracted from the residue by means of the mixed acids. [See, further, *J. Soc. Chem. Ind.*, 1920, 209A.] C. A. M.

Reaction of Tin Salts. A. Mazuir (*Ann. Chim. anal.*, 1919, [ii], **2**, 9).—The reaction depends on the insolubility of stannous or stannic iodide in sulphuric acid. Two c.c. of the neutral or slightly alkaline solution containing the tin salt are treated with 2 c.c. of 10% potassium iodide solution and 1 to 2 c.c. of concentrated sulphuric acid. A yellow, crystalline precipitate of tin iodide forms at once if the solution under examination contains not less than 0·1 gram of tin per litre; the precipitate is soluble in chloroform, alcohol, and dilute hydrochloric acid. It is decomposed by ether, iodine being liberated. Arsenic gives a similar reaction, but the arsenic iodide formed is insoluble in dilute or concentrated hydrochloric acid. In the case of antimony, the iodide obtained is flocculent and brick-red in colour. W. P. S.

Separation and Estimation of Lead and Bismuth. G. Luff (*Chem. Zeit.*, 1920, **44**, 71).—A nitric acid solution of the two metals is neutralised with ammonia, saturated ammonium nitrite solution and sodium nitrite solution are added, the mixture is

diluted to about 200 c.c., and boiled. When the evolutio nitrogen ceases, the precipitate (bismuth hydroxide or basic bisr nitrate) is collected on a filter, washed with hot water, then solved in nitric acid, the solution evaporated, and the residue igr and weighed as Bi_2O_3. The filtrate is acidified with acetic acid, the lead precipitated and weighed as lead chromate. The bisr oxide, after weighing, should be treated with nitric acid and hy fluoric acid, again ignited, and washed, to remove traces of s and alkali respectively. W. P.

The Estimation of Acetylene in Gaseous Mixtu J. A. MULLER (*Bull. Soc. chim.*, 1920, [iv], **27**, 69—71).— acetylene is absorbed in ammoniacal cuprous chloride, usir volume of gas containing at the most 10—11 c.c. of acetylene; solution is acidified with acetic acid, and the cuprous acetylic collected and washed. The paper and precipitate are transfe to a platinum crucible, and sulphuric acid is added drop by until a homogeneous fluid mass is obtained. The excess of is gently evaporated, and when fuming has ceased, the cru is heated to a red heat, cooled, and weighed. W. (

Determination of the Composition of Mixtures Alcohol and Water by Measurements of Electr Conductivity. I. M. KOLTHOFF (*Rec. trav. chim.*, 1920, 126—134).—For the determination of the alcohol content of or wine, the following procedure is recommended. The exces carbon dioxide is removed from the liquid by bubbling air thr it, and the liquid is then distilled with magnesium oxide. I c.c. of the distillate are mixed with 10 c.c. of approximately oxalic acid solution, and the mixture is made up to 100 with water. The specific conductivities x_1 and x_2 of the mix and of the original oxalic acid solution diluted to one-tenth water are then determined. Then $f_t = 100 \times x_1/x_2$. This can be corrected to f_{18} by means of the temperature-coefficient, ar table is given showing the relationship between f_{18} and the alc content of the distillate. W. (

Specific Reaction of Butylene βγ-Glycol and of Acetylmet carbinol, Products of Butyleneglycollic Fermentat LEMOIGNE (*Compt. rend.*, 1920, **170**, 131—132).—The chara isation of acetylmethylcarbinol in the products of microbic de position of sugars serves to differentiate certain groups of sir microbes, and the following method affords a ready mean detecting traces of this compound. The carbinol is oxidise diacetyl by means of ferric chloride, the diacetyl being distille and detected by precipitation in ammoniacal solution as ni dimethylglyoxime with a nickel salt and hydroxylamine. By method it is possible to detect acetylmethylcarbinol at a dilutio 1 in 1,000,000. The reaction is not given by any other of products of fermentation. W. (

Microchemical Method of Estimating Dextrose. II. IVAR BANG (*Biochem. Zeitsch.*, 1918, **92**, 344—347. Compare A., 1918, ii, 279).—It is found that the potassium iodate employed by the author in his modified method for the micro-estimation of sugar in blood does not keep well. He therefore uses free iodic acid instead. The *solution* is prepared by dissolving 0·3567 gram of pure potassium iodate in 10 c.c. of 20% sulphuric acid. 2·5 Grams of copper sulphate ($CuSO_4+5H_2O$) may also be added to it at the same time, and the solution is made up to 1 litre.

The author finds that by means of Willstätter and Schüchl's method, 0·1—0·5 mg. of sugar can be estimated. However, this method cannot be employed in the estimation of sugar in blood. *Blood containing* 0·107% *of sugar showed a content of* 0·22% and 0·23% by this method. S. S. Z.

Adsorption Compounds and Adsorption. V. The Adsorption Compounds of Cuprous Oxide. L. BERCZELLER (*Biochem. Zeitsch.*, 1919, **93**, 230—237).—In precipitating cupric hydroxide from cupric salts with sodium hydroxide, some of the alkali is adsorbed by the cupric hydroxide. The black hydroxides adsorb more of it than the blue ones. Iodate ions are also adsorbed by cupric hydroxide, but in this case the blue hydroxides adsorb more of it than the black. The presence of sugar prevents the adsorption of sodium hydroxide by cupric hydroxide. S. S. Z.

Estimation of Small Quantities of Sugar in the Presence of the Higher or Lower Products of Protein Degradation. ERWIN LAST (*Biochem. Zeitsch.*, 1919, **93**, 66—82).—The higher products of protein degradation, such as albumoses and peptones, the presence of which interferes with the estimation of sugar, can be removed by means of mercuric chloride *in neutral solution*. The sugar can then be estimated by Bertrand's method. In the presence of acids, the precipitation of these products is incomplete. An excess of mercuric chloride must also be avoided in order to ensure good results. *Two grams of mercuric chloride per gram of peptone* are found to be a suitable quantity. The presence of monoamino-acids does not affect the accuracy of the sugar estimation by Bertrand's method; ereptone, however, does influence the results. This is due to the special atomic grouping in ereptone, which, on boiling with alkali hydroxide, liberates ammonia, and this dissolves some of the cuprous oxide. Ereptone can be removed from sugar solutions also by precipitation with mercuric chloride in neutral solution. The removal of both the higher and lower products of protein degradation with mercuric nitrate according to the Patein-Dufau method conduces to accurate results. S. S. Z.

Estimation of Lactose in Altered Milks. E. HELDT (*Bull. Soc. chim.*, 1919, [iv], **25**, 617—621).—A more detailed account of work already published (compare A., 1919, ii, 84). W. G.

Modification of the Phenylhydrazine Method of Estimating Pentosans. PAUL MENAUL and C. T. DOWELL (*J. Ind. Eng. Chem.*, 1919, **11**, 1024—1025).—The material is distilled with sulphuric acid instead of hydrochloric acid, and the furfuraldehyde is estimated in the distillate by precipitating with a known excess of phenylhydrazine, filtering off the hydrazone, and determining the excess of phenylhydrazine in the filtrate. For this purpose, an aliquot part of the filtrate is heated with ammoniacal copper sulphate solution, and the nitrogen evolved is measured, the reaction previously employed by Ebler for the determination of hydrazine (A., 1906, ii, 53) being quantitative also in the case of phenylhydrazine. [See, further, *J. Soc. Chem. Ind.*, 1920, 170A.]

J. H. L.

A Microchemical Method for the Estimation of Acetone. M. RICHTER-QUITTNER (*Biochem. Zeitsch.*, 1919, **93**, 163—172).—A microchemical method in which 1—2 c.c. of urine and 1·5—3 c.c. of alkali need only be used. The urine is distilled once with steam in the presence of acetic acid, and a second time with dilute sulphuric acid. Blood or plasma need only be distilled once, and instead of the steam, air is passed through the heated flask. The titration of the distilled acetone is carried out with *N*/100-iodine and *N*/100-sodium thiosulphate. 0·1 Mg. of acetone in 100 c.c. can be estimated with accuracy by this method. The quantity of urine and blood used must contain not less than 0·04 mg. of acetone.

S. S. Z.

Microchemical Reactions of Veronal, Luminal, and Proponal. L. VAN ITALLIE and A. L. W. E. VAN DER VEEN (*Pharm. Weekblad*, 1919, **56**, 1112—1117; *J. Pharm. Chim.*, 1919, [vii], **20**, 337—343).—Small traces of the derivatives of barbituric acid separated from urine by treatment with lead acetate and hydrogen sulphide may be converted into an easily identifiable, crystalline form by sublimation. Veronal may be separated as monoclinic crystals from its solution in sodium hydroxide by the addition of an acid, potassium dichromate, or ammonium phosphate. Lead acetate gives an amorphous mass, which becomes crystalline on boiling. Ammoniacal silver nitrate gives an irregular, crystalline mass of large, simple crystals of veronal-silver. With thallium nitrate, crystals of veronal-thallium are formed. Luminal and proponal have only to be separated in the uncombined state. A crystal of ammonium phosphate introduced into a drop of a solution of these in sodium hydroxide causes the separation of the free acids in the form of drops which only gradually change into crystals, probably rhombic.

W. J. W.

Estimation of "Saccharin" in Urine. GEORGE S. JAMIESON (*J. Biol. Chem.*, 1920, **41**, 3—8).—Urine is treated with lead acetate and filtered. After acidifying with hydrochloric acid, the "saccharin" is extracted by ether, the ether removed by evapor-

ation, and the "saccharin" extracted from the residue by ether. The ether is removed, and the resulting residue is fused with sodium carbonate. From an estimation of sulphur in the fused product, the amount of "saccharin" may be deduced. J. C. D.

The Estimation of Aniline in Commercial Anilines. William James Sanderson and William Jacob Jones (*J. Soc. Chem. Ind.*, 1920, **39**, 8T).—A method of estimation is given which is based on a determination of the freezing point of the sample. The purity is deduced by reference to a table, which is provided, showing the freezing points of dry mixtures of aniline with varying proportions (1—7% by weight of the mixture) of each of benzene, phenylhydroxylamine, nitrosobenzene, *p*-aminophenol, nitrobenzene, *o*- or *p*-toluidine, *m*-phenylenediamine, and xylidine. J. K.

Formaldehyde Titration of Amino-acids in Aqueous Solutions or in Urine. W. Mestrezat (*Bull. Soc. Chim. Biol.*, 1919, **1**, 107—113).—The methods employed by Ronchèse (cited by Maillard, *Compt. rend. Soc. Biol.*, 1911, **61**, 653) are insufficiently accurate. J. C. D.

Urea and Hypobromite. L. Lescœur (*J. Pharm. Chim.*, 1919, **20**, 305—314, 343—351, 374—381).—The volume of nitrogen liberated by the action of alkaline hypobromite solution on urea is always less than that required by theory; too low results are also found if the urea is calculated from the amount of carbon dioxide formed or of the hypobromite used in the reaction. The deficit is to some extent dependent on the proportion of free alkali present, and decreases, but never quite disappears, as the quantity of free alkali is increased; it appears to be due to the conversion of a part of the urea into sodium cyanate. W. P. S.

Ureometer. P. Seyot (*Ann. Chim. anal.*, 1920, [ii], **2**, 11—13). —The apparatus consists of a graduated tube open at its lower end, whilst the upper end, above the zero point, is bent over and downwards for a short distance, where it is blown out to form a bulb. A short side-tube with a tap is provided at the top of the bend. The bulb has a tubulure at the side into which is ground the neck of a small cylindrical bulb. The latter contains the hypobromite solution, whilst the urine or other liquid under examination is placed in the larger bulb. The whole apparatus is placed in a cylinder of water, the level of the latter then adjusted to the zero point by manipulating the tap, and the smaller bulb then turned (by means of the ground-in joint) so that the hypobromite solution mixes with the urine in the larger bulb. The evolved nitrogen displaces water from the graduated tube, and the volume of the nitrogen is noted after the water-level has been adjusted. If 1·3 c.c. of urine is taken for the estimation, each c.c. of nitrogen is equivalent to 1 gram of urea per litre of urine. W. P. S.

Identification of Traces of Hydrocyanic Acid. L. CHELLE (*Bull. Soc. Pharm., Bordeaux*, 1919; from *Ann. Chim. anal.*, 1920, [ii], **2**, 21—24. Compare A., 1919, ii, 529).—The following tests may be used for the identification of traces of hydrocyanic acid: *Phthalein test.*—A red coloration is obtained when a cyanide solution is treated with a drop of alkaline phenolphthalein solution reduced previously with zinc, and a drop of 0·1% copper sulphate is added. iso*Purpurate test.*—If a cyanide solution is heated with the addition of alkaline picric acid solution, an orange coloration develops after a few hours. *Ammoniacal silver iodide test.*—The reagent is prepared by diluting a mixture of 10 c.c. of $N/1000$-silver nitrate solution, 2 c.c. of ammonia, and five drops of 19% potassium iodide solution to 100 c.c.; this reagent gives a turbidity with a cyanide solution. For instance, if a turbidity is obtained when 1 c.c. of the cyanide solution is treated with 0·2 c.c. of the reagent, less than 0·001 mg. of hydrocyanic acid is present; with 0·005 mg. of hydrocyanic acid, 1 c.c. of the reagent is required. *Ferrocyanide test.*—This is the most characteristic reaction of hydrocyanic acid; it may be used for the identification of hydrocyanic acid in silver cyanide and mercuric cyanide. W. P. S.

Sensitiveness of some Cyanide Reactions. JOHN B. EKELEY and ICIE C. MACY (*Proc. Colorado Sci. Soc.*, 1919, **11**, 269—274).—Working directly with solutions of potassium cyanide, the Prussian blue test gives positive results (a blue precipitate on keeping) at a dilution of $1:7\times10^4$ (at about $1:17\times10^4$ for hydrogen cyanide). One hundred c.c. of potassium cyanide solution ($1:7\times10^5$) give a definite result after acidifying with 10 c.c. of 1% tartaric acid and distilling off about 2 c.c.; this corresponds with a dilution of hydrogen cyanide about $1:1{\cdot}7\times10^6$. The hanging-drop method with silver nitrate gives positive results with solutions of potassium cyanide ($1:8\times10^6$, corresponding with hydrogen cyanide at a dilution of about $1:19\times10^6$) when 100 c.c. are exposed to the drop of silver nitrate for fifteen minutes. The Schönbein test gives positive results with potassium cyanide solutions at a dilution of $1:18\times10^6$ in the light and $1:23\times10^6$ in the dark (equivalent to $1:43\times10^6$ and $1:55\times10^6$, respectively, for hydrogen cyanide). This test should be performed in closed vessels in the dark to secure trustworthy results, and only at extreme dilutions does it indicate the presence of hydrogen cyanide and exclude the presence of other substances (chlorine, bromine, hydrogen peroxide, hydrogen chloride) which are known to respond at high concentrations. CHEMICAL ABSTRACTS.

Estimation and Separation of Pyridine and Ammonia. E. B. R. PRIDEAUX (*Trans. Faraday Soc.*, 1919, **15**, 137—147).—Precise information as to the conditions for the titration of pyridine and of ammonia in the presence of pyridine, and of the separation of the two by distillation, has been obtained by application of the electrochemical theory. Congo-red is the correct

ndicator for pyridine, and nitric acid the best acid. A correct ndicator for the titration of ammonia in the presence of pyridine s α-naphtholphthalein. Both ammonia and pyridine are estimated vith sufficient accuracy provided that pyridine is not present in excess. Rosolic acid may be used if the bases are titrated directly, and the pyridine is present in amount considerably less than the ammonia. Ammonia and pyridine may be partly separated by listillation from a solution of which the acidity is maintained at about $p_H = 3$ to 4 (reddish-brown to Congo, orange to methyl-orange). The first part of the distillate contains most of the pyridine, the second most of the ammonia, so that the titrations ust described may be used. J. R. P.

Estimation of Indole in Biological Media. HARPER F. ZOLLER (*J. Biol. Chem.*, 1920, **41**, 25—36).—The usual preliminary team distillation of the indole solution is abandoned and replaced y direct distillation, care being taken to have the solution adjusted o a hydrogen-ion concentration of p_H 9·2 (see this vol., i, 250). The distillation is continued until all but about 10 c.c. have been lriven over, the distillate being collected in a 100 c.c. volumetric lask and made up to the mark. A portion of the distillate con-aining not more than 0·20 mg. of indole is measured into a test-ube of convenient size, and two drops of 1·0% solution of sodium itrite and five drops of concentrated sulphuric acid are added. The tube is shaken and left for five minutes for the nitroso-reaction o approach equilibrium. The contents are then extracted with hree portions of 3 c.c. of *iso*butyl or *iso*amyl alcohol, each portion eing drawn off with a pipette and placed in a test-tube having a 0 c.c. graduation. *iso*Butyl or *iso*amyl alcohol is then added to ring the contents of the tube up to 10 c.c., and the colour is natched against a series of standards prepared by similar treat-nent of solutions containing a known amount of pure indole.

The method is stated to be simple, trustworthy, and rapid. The elative sensitivities of Herter's naphthaquinone reaction and the itroso-reaction were found to be 1:2,000,000 and 1:1,500,000 espectively.

A warning is sounded against the use of the vanillin test pro-osed by Steensma (A., 1906, ii, 315).

The rate at which the equilibrium of the nitroso-indole reaction reached depends on the factors of concentration and temperature. At temperatures from 30—90°, the full depth of colour is obtained n a few seconds, but higher temperatures tend to destroy the oloured compound when in aqueous solutions. In pure *iso*butyl lcohol the colour is not destroyed by heating for several hours at 00°. In actual analyses, the test should not be carried out at emperatures above 30°. J. C. D.

Detection of other Cinchona Alkaloids in Salts of Quinine. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 451—459).—Kerner nd Weller's method has many disadvantages, and only gives

accurate results under certain conditions. The following method is suitable for quinine sulphate, but is inapplicable to other salts. 0·5 Gram of quinine sulphate is boiled gently for one minute with 250 mg. of sodium sulphate and 10 c.c. of water. Water is then added to restore the original volume, and the mixture cooled to 15°, with shaking. The liquid, with the precipitate, is kept below 18° for twenty-four hours, and then filtered through glass wool. Three drops of 4*N*-sodium hydroxide are added to the filtrate, which is then heated on the water-bath for half an hour. After twelve hours, the solution is examined for the presence of a precipitate. The test is sensitive to 1% of cinchonidine. In regard to the nitroprusside test, the author does not confirm Kruysse's opinion of its sensitiveness, and failed to devise a means of increasing this. De Vrij's chromate test is considered to be a suitable substitute for Kerner and Weller's method. For quinine bisulphate, 0·5 gram is boiled with 20 c.c. 2*N*-sodium acetate until the liquid is clear. Then 3 c.c. of 10% potassium chromate are added, and further treatment is carried out by de Vrij's method. For quinine, 0·5 gram is taken, together with 3 c.c. of *N*-sulphuric acid and 20 c.c. of 2*N*-sodium acetate, and the test continued as above. Quinine hydrochloride may be tested exactly as described by de Vrij.

W. J. W.

Estimation of Albumin in Urine. OTTO MAYER (*Zeitsch. anal. Chem.*, 1919, **58**, 337—346).—A reagent described previously by the author (A., 1914, ii, 80) for the estimation of albumin in urine is altered in composition in order to render it more sensitive. Ten grams of mercuric chloride, 65 grams of sodium chloride, and 25 grams of citric acid are dissolved in 500 c.c. of hot water and the solution is filtered after a few days. This solution will give a ring reaction in about ten minutes with as little as 0·0002% of albumin, whilst 0·001% of albumin is denoted by the appearance of a turbid zone within three minutes. If the urine contains more than 0·001% of albumin, the test is repeated after dilution until the reaction is just observable, and the quantity of albumin present then calculated from the degree of dilution. W. P. S.

Estimation of Catalase in Blood. MEYER BODANSKY (*J. Biol. Chem.*, 1919, **40**, 127—130).—In making estimations of catalase by the method employed by Burge (*Amer. J. Physiol.*, 1916, **41**, 153), it was found that different samples of hydrogen peroxide often gave results which differed by 15—35%. It was experimentally shown that the reaction of the medium is one important factor in determining the activity of catalase. Consequently, caution must be exercised in maintaining uniform conditions when a series of determinations are being made. J. C. D.

General and Physical Chemistry.

The Optics of Disperse Systems. IV. I. Lifschitz and Georg Beck (*Kolloid Zeitsch.*, 1920, **26**, 58—66. Compare A., 1918, ii, 181, 253; this vol., ii, 137).—The chemical processes occurring during change in the colloidal state and their effect on the change in the light absorption is theoretically considered. An attempt is made to use the published work on the refractometric measurements of colloids to explain the rôle of the change in the colloidal state in the change in light absorption. The density, refractive index, molecular and specific refractivities for the C, D, and F lines have been measured for solutions of twenty organic acids and their sodium salts in methyl alcohol at 25°. It is shown that the increase in refraction from acid to sodium salt is different in the different cases, but with acids which form salts accompanied by a rearrangement or by exercising subsidiary valencies there is an extraordinarily large change. The increase in refraction in salt formation is independent of simultaneous peptisation or colloid formation, and an abnormally large increase in the refraction cannot be explained by a change in the dispersity. It is also shown that a very large percentage of cases of vario-chromism and polychromism are to be explained by intramolecular action of subsidiary valencies, and that chromoisomerism is to be similarly explained. J. F. S.

Influence of Position and Accumulation of Substituents on Spectrochemical Behaviour. V. Alkyloxyacetic Acids. A. Karvonen (*Acad. Sci. Fennicae*, 1916, [*A*], **10**, No. 8, 1—7; from *Chem. Zentr.*, 1919, iii, 987. Compare this vol., ii, 129).—The alkyloxyacetic acids exhibit optical values slightly lower than that of acetic acid itself. H. W.

Influence of Position and Accumulation of Substituents on Spectrochemical Behaviour. VI. Esters of Keto-alcohols, COMe·[CH$_2$]$_n$·O·CO·Me. A. Karvonen (*Acad. Sci. Fennicae*, 1916, [*A*], **10**, No. 8, 1—7; from *Chem. Zentr.*, 1919, ii, 987).—Further investigation with fresh materials shows that the optical values increase somewhat with increase in the relative distance between the carbonyl group and that of oxygen connected to two carbon atoms in the cases of esters of the lower alkyloxy-aliphatic acids and keto-alcohols. H. W.

Influence of Position and Accumulation of Substituents on Spectrochemical Behaviour. VII. Ether-Alcohols, RO·[CH$_2$]$_n$·OH. A. Karvonen (*Acad. Sci. Fennicae*, 1916, [*A*], **10**, No. 9, 1—8; from *Chem. Zentr.*, 1919, iii, 981).—Spectrochemical investigation of the monomethyl, ethyl, and propyl ethers

of ethylene glycol and of the monomethyl and ethyl ethers of trimethylene glycol shows these compounds to be closely related optically. H. W.

Influence of Position and Accumulation of Substituents on Spectrochemical Behaviour. VIII. Mutual Spectrochemical Action of Hydroxyl Groups. A. KARVONEN (*Acad. Sci. Fennicae*, 1916, [*A*], **10**, No. 10, 1—10; from *Chem. Zentr.*, 1919, iii, 981).—Investigation of ethylene and trimethylene glycols showed that two hydroxyl groups in direct union with one another cause marked exaltation, which is progressively diminished by the successive introduction of methylene groups between the hydroxyls. Certain atoms or atomic groups directly united with one another cause optical exaltation (HO$\leftarrow\rightarrow$OH, O$\leftarrow$ $\rightarrow$O, -S$\leftarrow$ $\rightarrow$S-, -Se$\leftarrow$ $\rightarrow$Se-), whilst others bring about depression

$$(C\rightarrow \leftarrow(OR)_{2,3,4}, H_2N\rightarrow \leftarrow NH_2, N\rightarrow \leftarrow N),$$

a third section being neutral or nearly so ($H_2N \rightleftharpoons OH$). This action cannot readily be ascribed to supplementary valencies, and not invariably to the existence of double bonds between the atoms. H. W.

Effect of an Electric Field on the [Spectrum] Lines of Argon and Oxygen. E. BÖTTCHER and F. TUCZEK (*Ann. Physik*, 1920, [iv], **61**, 107—112).—The effect of an electric field of 26,000 *V/cm* on the spectrum lines of argon, and on both the spark and arc lines of oxygen, has been investigated. In the case of argon, the lines are absolutely unaffected by the field; the same result was obtained with the spark lines of oxygen. Of the arc lines the 3—7 members of the I subsidiary triplet series showed a displacement towards the red which increased with increasing member number. The four lines λλ 4846, 4743, 4634, and 4559 are observed in the spectrum under the influence of the field, and have not before been observed. They are displaced toward the violet. The intensity increases with increasing wave-length, and the series ceases with the most intensive member without any indication of a further less intensive member. The *p*-components are considerably more intensive than the *s*-components. With increasing strength of field the intensity of the lines with longer wave-lengths increases more rapidly than that of those with shorter wave-lengths. The lines are regarded as belonging to a sharp subsidiary series of the I triplet subsidiary series. J. F. S.

Spectro-analytical Investigation of the Luminosity of Decomposing Ozone. KARL STUCHTEY (*Zeitsch. wiss. Photochem.*, 1920, **19**, 161—197).—The spectrum of the luminosity of an oxygen–nitrogen mixture in an ozoniser has been photographed and shown to be made up of the second positive group of the nitrogen spectrum, the emission spectrum of the *Y*-oxide of nitrogen (Warburg and Leithäuser, A., 1906, ii, 743; 1907, ii, 342;

spectra. On heating ozone at 400° in a specially constructed oven a strong luminosity is observed. The light shows both the visible and the ultra-violet spectra of ozone. A mixture of nitrogen and ozonised oxygen heated in the same furnace shows, in addition to the emission spectrum of ozone, also the emission spectrum of the Y-oxide of nitrogen. An explanation of the mechanism of the luminosity is given, and it is shown that the luminosity does not depend on presence of oxidisable substances. J. F. S

A Helium Series in the Extreme Ultra-violet. THEODORE LYMAN (*Nature*, 1919, **104**, 314; *Science*, 1919, **50**, 481—483).—By using a powerful disruptive discharge in helium a fairly strong line, in addition to those previously reported for the helium spectrum, was found to appear at wave-length 1640·2, and a fainter line at about 1215·1. Experimental evidence is thus afforded for the existence of the lines 1640·1 and 1214·9 as calculated from theoretical considerations. CHEMICAL ABSTRACTS.

Some New Spark Spectra in the Extreme Ultra-violet. LÉON BLOCH and EUGÈNE BLOCH (*Compt. rend.*, 1920, **170**, 320—322).—Using the spectrograph with a fluorspar prism, previously described (*ibid.*, 226), the authors have studied the spectra from a condensed spark between metallic electrodes in hydrogen in the case of four metals. Cadmium gave a spark spectrum extending to $\lambda = 1500$, and the rays have been measured down to $\lambda = 1600$. Bismuth gave a spectrum to $\lambda = 1500$, the rays being measured to $\lambda = 1550$. The spark spectrum of nickel is very rich in rays in the extreme ultra-violet, these being measured to $\lambda = 1540$. Down to $\lambda = 1650$ there is a great similarity between the arc and spark spectra. For silver the rays were measured down to $\lambda = 1496$. Nickel gave a doublet, $\lambda = 1550·7$ and 1548·2, and silver gave a doublet, $\lambda = 1551·3$ and 1548·7. W. G.

Line Spectra of Cadmium and Zinc in the Electrodeless Ring Discharge. A. HAGENBACH and H. SCHUMACHER (*Zeitsch. wiss. Photochem.*, 1919, **19**, 129—142).—The spectra of zinc and cadmium produced from an electrodeless discharge have been measured and compared with the arc and spark spectra of these elements. It is shown that the spectrum coincides neither with the arc spectrum nor with the line spectrum in either case, but contains lines of both spark and arc spectra as well as a number of new lines. The intensity of the various lines is also very different from that of the lines in the arc and spark spectra. In the case of cadmium, lines are measured from λ 6467·4 to 2183·1, and forty-four new lines lying between λ 5511·0 and 2436·25 are recorded both in the international system and in Rowland's system. In the case of zinc, the lines measured lie between λ 6362·58 and 2252·87 and thirteen new lines lying between λ 3186·24 and 2246·88 are recorded. It is also shown that under suitable conditions a band spectrum can also be obtained. J. F. S.

Band Spectrum of Zinc from the Electrodeless Ring Discharge. A. HAGENBACH and H. SCHUMACHER (*Zeitsch. wiss. Photochem.*, 1919, **19**, 142—148. Compare preceding abstract).—The band spectrum of zinc obtained from an electrodeless discharge has been measured over the range λ 4894·9—3469·5, and compared with existing measurements. A large number of new bands are recorded. J. F. S.

Measurement of the Arc Spectrum of Iron below λ 2373 according to the International System. H. SCHUMACHER (*Zeitsch. wiss. Photochem.*, 1919, **19**, 149—158).—The iron spectrum of smaller wave-length than λ 2373 has been photographed and measured. The wave-lengths are given on the international system, and an accuracy of about 0·03 Å. is claimed for the values. As source of light an iron arc burning with 4 amperes and 220 volts was used. The values are compared with those of Kayser and Runge. J. F. S.

Theory of Absorption Spectra. I. LIFSCHITZ (*Schweiz. Chem. Zeit.*, 1918, **2**, 58; from *Chem. Zentr.*, 1919, iii, 970).—A reply to Kauffmann's criticisms (A., 1917, i, 391) of the author's views (A., 1917, ii, 435). H. W.

The Chromophore Function. V. Optical Properties of some Heavy Metal Complexes. I. LIFSCHITZ and ERNST ROSENBOHM (*Zeitsch. wiss. Photochem.*, 1920, **19**, 198—214. Compare A., 1917, ii, 62, 435).—The absorption spectra of the heavy metal complexes consist in general of at least three bands which lie between λ 6000 and λ 2000 Å. units. Of these, that with the longest wave-length depends mainly on the nature of the central atom; the next band depends on the nature of the co-ordinated groups if the central atom is the same. The band with shortest wave-length is not so completely investigated, because in many cases it lies so far in the ultra-violet as to be unmeasurable with the apparatus employed. All the work on the subject tends to show that this band is displaced more toward the longer wave lengths in the presence of bivalent co-ordinated groups than in the presence of univalent groups. J. F. S.

Calculation of the Frequency Limits of Absorption K and L of the Heavy Elements. LOUIS DE BROGLIE (*Compt. rend.*, 1920, **170**, 585—587).—For tungsten, platinum, gold, lead, bismuth, thorium, and uranium examined, Vegard's formula gives results for the frequency limits of absorption, *K* and *L*, which are much more nearly in agreement with the mean of the observed results than those calculated by Bohr's formula. W. G.

Absorption Coefficients of Solutions for Monochromatic Radiation. E. O. HULBURT and J. F. HUTCHINSON (*Carnegie Inst. Pub.*, 1918, **260**, 6—69).—The absorption-coefficient of solutions of inorganic salts in water and in different alcohols has been

measured at intervals of 20 $\mu\mu$ to 40 $\mu\mu$ throughout the spectrum region from 600 $\mu\mu$ to 1300 $\mu\mu$. For each salt a series of solutions varying in concentration from saturation to moderate dilution was prepared, and the absorption curve drawn for each solution. The molecular absorption-coefficient, A, of the salt was calculated for each wave-length and plotted against c, the concentration of the salt in gram-molecules. Solutions of cobalt chloride in water, ethyl, propyl, *iso*butyl, and *iso*amyl alcohols were examined by the photographic method; the values of A changed with the concentration, and the absorption curves for the higher alcohols were similar to those for ethyl alcohol. The following solutions were also examined: cobalt nitrate and sulphate, nickel chloride (anhydrous and the hexahydrate), nitrate and sulphate in methyl, ethyl, and propyl alcohols; ammonium ferric alum in water; chromic chloride, nitrate, and sulphate; and potassium permanganate. The relation between A and c has been determined from the data thus obtained. In general, A is not constant. Sometimes it decreases with dilution, in other cases increases with dilution, and also passes through a minimum; a maximum was not obtained. The deviations of A from a constant value were usually small, except at certain points in the spectrum, which in general were situated at the edges of absorption bands.

No theory adequately explains the observations.

CHEMICAL ABSTRACTS.

Colour Antagonism or Chemical and Electrical Polarity of the Spectrum. GABRIELE RABEL (*Zeitsch. wiss. Photochem.*, 1919, **19**, 69—128).—The long-wave half of the spectrum from the yellowish-green to the infra-red is termed positive light, whilst the short-wave half from bluish-green to ultra-violet is termed negative light. It is shown that phosphorescent light is produced by negative light and extinguished by positive light. Phosphorescent substances and certain classes of organic substances change their colour when subjected to negative light, but in positive light regain the original colour. Silver salts are reduced by negative light, but are oxidised by positive light. Certain biological and chemical reactions occur in the reverse direction in negative light from that in positive light. Electrodes which are sensitive to light undergo opposite potential changes in negative light from those in positive light. The retina of the eye belongs to the light sensitive electrodes. The movements of lower organisms are influenced in opposite ways by positive and negative light. In high-tension discharge in hydrogen, in the red hydrogen layers, the maximum potential lies in the luminous layer, the minimum in the dark space between the layers, whilst with the blue hydrogen layers the maximum is in the dark space and the minimum in the luminous layer. In the bluish-red double layers the dark space shows neither maximum nor minimum, but is positive to the blue layer and negative to the red layer. If a plate covered with sodium chloride is brought into a luminous layer discharge, reduction (that is, formation of a blue

coloration) occurs in the luminous layer in the blue discharge, and in the dark space in the red discharge. J. F. S.

Fluorescence and Absorption of the Uranyl Sulphates. E. L. NICHOLS and H. L. HOWES (*Physical Rev.*, 1919, [2], **14**, 293—305).—The fluorescence spectrum of the uranyl sulphates consists of eight equidistant bands, the first and eighth of which disappear at the temperature of liquid air. The remaining bands are resolved into groups of narrow line-like bands, the homologous members of which form series having constant frequency intervals, ranging from 85·7 in $UO_2SO_4,Cs_2SO_4,2H_2O$ to 83·0 in

$$UO_2SO_4,K_2SO_4,2H_2O.$$

The fluorescence groups are distinguished by a strong pair of bands about eight frequency units apart and several weak bands, some of which are doublets. There is a shift of all bands towards the violet, with increasing molecular weights, of about fifteen frequency units in passing from the spectrum of uranyl sulphate to that of the cæsium double salt. The absorption spectra of the sulphates are made up of series of bands having a frequency interval of 70·3 on an average. These absorption series extend into group 7 of the fluorescence without break of interval. There are many reversals where fluorescence and absorption overlap. The reversing region is, therefore, one group further towards the red than in most spectra of the uranyl compounds. CHEMICAL ABSTRACTS.

Fluorescence and Absorption of the Uranyl Acetates. E. L. NICHOLS, H. L. HOWES, and FRANCES G. WICK (*Physical Rev.*, 1919, [2], **14**, 201—221).—The paper deals with the fluorescence and absorption spectra of the two known forms of uranyl acetate and of thirteen double uranyl acetates as they appear when excited at the temperature of liquid air. The essential identity of the spectra of the double acetates of lithium, potassium, calcium, manganese, and strontium, both as regards the location of the principal bands and the structure of the fluorescence groups, is established and the deviations from this type occurring in the spectra of the uranyl acetates containing barium, ammonium, rubidium, sodium, magnesium, zinc, silver, and lead are considered. The approximate identity of frequency intervals for all series and for all salts is likewise established, the interval being 84·76. CHEMICAL ABSTRACTS.

Quanten Theory Basis of Photochemistry. E. WARBURG (*Zeitsch. Elektrochem.*, 1920, **26**, 54—59).—A theoretical paper in which it is shown that every photochemical reaction is characterised by the specific photochemical action ϕ, that is, by the number of gram cals. of heat absorbed per mol. The fundamental law of photochemical reaction is, that energy of frequency ν is absorbed in quanta by the reacting molecules. The molecules which absorb the light radiation are termed "photochemical reserved molecules," and from the law stated, the number of these may be calculated. Valency radiation is the radiation which in the reserving

of 1 mol. of the photolyte is absorbed by it. The indicated photochemical equivalent (p) is the number of mols. which are reserved in the absorption of 1 gram-cal. The effective photochemical equivalent is the number of mols. which are decomposed or changed by the absorption of 1 gram-cal. It is equal to the specific photochemical action ϕ when this is calculated on the number of decomposed or changed molecules. ϕ/p is the efficiency relationship. Einstein's photochemical equivalent law says that every absorbing or reserved molecule is by the act of absorption decomposed or changed, and when the secondary processes are known it determines the efficiency relationship for which values $\leqq 1$ are obtained. The law is rigidly held in isolated cases only, because in general the reserved molecules, or at least a part of them, do not undergo primary change for the following reasons: (1) the valency radiation is smaller than the molecular decomposition energy; (2) energy is lost during the absorption of the radiation; and (3) the chemi-cal change only takes place as a secondary process as in the case of photolytic isomerisation. J. F. S.

Photochemical Studies. VIII. Periodic Light Reactions. JOH. PLOTNIKOW (*Zeitsch. wiss. Photochem.*, 1919, **19**, 22—39).—The action of chlorine on α-cyanocinnamic acid in carbon tetrachloride solution under the influence of light of wave-length $\lambda = 436\ \mu\mu$ has been investigated at 17°. It is shown that there is no formation of a chlorine additive compound, and that the nitrile concentration has no influence on the reaction, but chlorine is used up linearly with time, and its use is due to a hitherto unknown reaction between carbon tetrachloride and chlorine. The reaction between carbon tetrachloride and chlorine was therefore investigated. It is shown that the absorption of chlorine is linear both with blue light $\lambda = 436\ \mu\mu$ and ultra-violet light $\lambda = 366\ \mu\mu$. Using the whole of the light from a uviol lamp, a periodic change in the concentration of the chlorine is observed. Further experiments show that in light, pure carbon tetrachloride yields free chlorine. The reaction is discussed, and the possibility of periodic light reactions shown. Two types of such reactions are indicated: (1) Periodic light reactions are a necessary consequence of the stationary condition of photochemical processes, and must occur periodically so long as light of various wave-lengths acts. (2) Periodic light reactions are the result of the combination of different opposing reactions, which are brought into existence by light of different wave-lengths, and are influenced by different catalysts, and consequently tend to an equilibrium condition. J. F. S.

Photochemical Studies. VII. Equilibria in Photochemical Addition of Bromine. JOH. PLOTNIKOW (*Zeitsch. wiss. Photochem.*, 1919, **19**, 1—21).—Reactions of the type

$$CR^1R^2{:}CR^3R^4 + Br_2 = CR^1R^2Br{\cdot}CR^3R^4Br$$

are reversible, and are of such a nature that the equilibrium position, in the dark as well as in the light, depends on the temperature,

concentration, nature of the solvent, intensity of light, and the nature of the radicles R^1, R^2, R^3, and R^4. The reaction between bromine and α-cyanocinnamic acid in light has been investigated: $CHPh\colon C(CN)\cdot CO_2H + Br_2 \rightleftharpoons CHPhBr\cdot CBr(CN)\cdot CO_2H$. The reactions were carried out in carbon tetrachloride solution, using light of wave-length $\lambda = 436\,\mu\mu$ at 7°. It is shown that bromine does not react as Br_2, but as 2Br, and the reaction taking place is proportional to the square of the absorbed light energy. The displacement of the equilibrium is proportional to the light intensity. The *equilibrium formula for the reaction has the form*

$$Q = J(1 - e^{-ip(b-y)^2(a-y)})/py,$$

where y is the equilibrium constant of the dibromide, p the thickness of the layer of solution, a the initial concentration of the nitrile, b the initial concentration of the bromine, i the normal light absorption constant of bromine (for $\lambda = 436\,\mu\mu$ it is 0·2156 per millimol. concentration), and J the light intensity. The temperature-coefficient of the dark reaction of the dibromide decomposition is determined from the corresponding equilibrium displacement and found to be 2·14. It is suggested that the extreme ultra-violet rays have the opposite action to the long waves on this reaction.

J. F. S.

Spectral Photoelectric Sensitivity of Silver Sulphide and several other Substances. W. W. Coblentz and H. Kohler (*Bull. Bur. Standards*, 1919, **15**, 231—249; *Sci. Paper*, 1919, No. **344**).—Data are given of the change in the electrical resistance of the sulphides of silver and bismuth when exposed to radiations from 0·6 μ in the visible spectrum to 3 μ in the infra-red. Galena, cylindrite, pyrites, and jamesonite did not show photoelectric sensitivity for the highest spectral radiation intensities available. The sulphides of silver and bismuth are sensitive from 0·6 μ to 1·8 μ. The photoelectric response for silver sulphide becomes fatigued at the ordinary temperature. The change in resistance of the crystal when exposed to radiation is first negative and then positive, the resultant change being negative and approximately one-fifth of the original change. At −158° this polarisation phenomenon disappears, and the response to radiation is the same as that of other substances, such as selenium or molybdenite. The sensitivity is greatly increased when the temperature is lowered to −158°. The sensitivity curve is quite symmetrical, and shows a maximum at 1·2 μ. An increase in the intensity of the exciting radiation shifts the maximum towards the long wave-lengths.

A spectral photoelectric sensitivity curve of bismuthinite was obtained at −166°, maxima occurring at 0·64 μ and 1·08 μ.

Chemical Abstracts.

Photo-oxidation of Organic Compounds by Chromates. Joh. Plotnikow (*Zeitsch. wiss. Photochem.*, 1919, **19**, 40—56).—The photo-oxidation of ethyl alcohol of various concentrations by *ammonium chromate* and *ammonium dichromate* in light of wave-

length $\lambda=436\,\mu\mu$ has been studied at 20°. It is shown that the velocity constant may be calculated by means of a linear equation, and that it is proportional to the concentration of the alcohol. Increase in the salt concentration causes the reaction velocity to approach a maximum. The absorption constants of the salt solutions have been measured, and are found to be a function of the alcohol concentration and show a maximum. The dichromate follows Beer's Law, but the chromate does not. The absorption changes brought about by the alcohol do not affect the reaction velocity. The velocities of oxidation are the same with chromate as with dichromate. The temperature-coefficient of the reactions is 1·02. These reactions in general exhibit a perfectly normal photochemical behaviour. J. F. S.

Biochemical Action of Light. F. SCHANZ (*Pflüger's Archiv*, 1918, **170**, 646—676; from *Physiol. Abstr.*, 1918, **3**, 552).—Observations on the lens of the eye have shown that the effect of light is to render protein less soluble. Some authors have attributed this change to certain substances accompanying the protein. The presence of acetone in diabetes coupled with the frequent occurrence of lenticular opacity suggested a series of experiments in which equal amounts of a protein solution in a series of quartz tubes were treated with increasing amounts of acetone. Series 1 and 2 were placed in the sunshine, whilst series 3 was incubated in the dark at 38°. After four days the contents of the various tubes were equalised by appropriate additions of acetone, the only distinction being that in series 1 and 3 the added acetone had been previously treated with light, whereas in series 2 it had not. The amount of precipitation, after the addition of ammonium sulphate, sodium chloride, and acetic acid by the method previously described, was then noted in each case. The results showed that the change from a more to less soluble condition of the protein was due to the effect of light on the protein itself; the reaction was, however, increased by the presence of acetone. The amount of acetone breakdown (amount of gas formed) was tested after exposure to a quartz lamp of acetone (1) in ordinary glass (absence of shorter rays than $\lambda\,30\,\mu\mu$); (2) in quartz (absence of shorter rays than $\lambda\,200\,\mu\mu$); and (3) shaded with a "euphos" glass screen (rays shorter than $\lambda\,400\,\mu\mu$). The results showed that acetone absorbed and was acted on by the ultra-violet rays alone. The author maintains that chemically pure organic salts are quickly broken down by the action of light in the absence of iron. Some quartz spectrographs figured in the text show absorption of the violet rays by protein and other substances, the greatest absorption being exhibited by acetaldehyde and acetone. Certain coloured substances, such as eosin, hæmatoporphyrin, and chlorophyll, act as optical sensitisers; eosin is non-toxic unless the organism is exposed to intense light. Mice die suddenly if exposed to daylight after previous injection of hæmatoporphyrin, and various lesions of the skin occur in sub-acute cases. It is suggested that the brilliant

colourings of flowers, etc., is to enable the organism to select the particular light rays required. Other experiments show that the growth of plants is affected by ultra-violet rays. J. C. D.

The Reaction of Proteins to Light. F. SCHANZ (*Pfluger's Archiv*, 1917, **169**, 82—86; from *Physiol. Abstr.*, 1917, **2**, 584).—The author refers to his previous work on the lens proteins, and also to Neuberg's work. Proteins are more sensitive to light than Neuberg considers, and experiments are given which show that quartz lamp rays can effect in them changes in solubility, etc., so that albumins then show the characters of globulins. J. C. D.

Some Observations on the Action of Coal on a Photographic Plate. ERIC SINKINSON (T., 1920, **117**, 165—170).

Chemical Actions of Radiation. EUGÈNE WOURTZEL (*Le Radium*, 1919, **11**, 289—298, 332—347. Compare A., 1914, ii, 18, 238).—The chemical action of α-rays from radium emanation on hydrogen sulphide, ammonia, nitrous oxide, and carbon dioxide has been investigated. When the reaction is not accompanied by secondary reactions, it is found that the amount of decomposition, under the same conditions of volume, pressure, and temperature, is proportional to the amount of emanation present. This is the case with the reactions $H_2S = H_2 + S$ and $NH_3 = N + 3H$. The effect increases with the dimensions of the vessel, and the volume, but tends to a maximum value, corresponding with the total utilisation of the energy of the radiation. If K, K_∞ are the velocity constants for particular conditions and for total utilisation of energy respectively, R is the radius of the vessel, and p the pressure, then, when $K > 0{\cdot}5K_\infty$, it is found that $K = K_\infty(1 - C/Rp)$, where C is a constant. When $K < 0{\cdot}5K_\infty$, the relation is represented by a line tangent to the above curve, and passing through the origin. The decomposition of nitrous oxide is complicated by a secondary reaction, namely, the formation of nitric peroxide from the nitric oxide and oxygen set free in the initial reactions $N_2O = N_2 + O$; $N_2O = NO + N$. Contrary to the statement of Ramsay and Cameron, carbon dioxide is only very slowly decomposed by α-rays. No theoretical conclusions are drawn from the results beyond the statement that the decompositions do not follow Faraday's law. A full account of the apparatus used is given. J. R. P.

New Arrangement for the Röntgen [Ray] Crystallographic Investigation of Crystalline Powders. HELGE BOHLIN (*Ann. Physik*, 1920, [iv], **61**, 421—439).—A new arrangement is described, in which by means of a cylindrical arc-shaped scattering surface, made of a compressed, crystalline powder, interference lines can be produced. One edge of the lines is sharp and may be geometrically defined, whereby an increased accuracy over that of the previously described methods is rendered possible. It is shown that the sharpness and the position of the line edge is in-

dependent of the width of the slit and of the depth to which the radiation penetrates. By means of photographs of the interference lines the space grating of thorium, nickel, and magnesium has been determined by this method. It is shown that thorium and nickel have face-centred cubic lattices, whilst magnesium has a lattice made up of two simple interpenetrating hexagonal lattices. J. F. S.

An Experimental Determination of the Critical Electron Velocities for the Production of the Ionisation and Radiation on Collision with Argon Atoms. FRANK HORTON and ANN CATHERINE DAVIES (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 1—23. Compare A., 1919, ii, 210).—In the conclusion of Franck and Hertz that ionisation occurred in argon when the velocity of the colliding electrons was raised to 12 volts, the ionisation of the gas could not be distinguished from photoelectric effects of radiation produced by the collisions. By methods similar to those previously employed for helium, it has been shown that, when electrons bombard argon atoms, a radiation is produced when the electrons attain a velocity corresponding with 11·5 volts, which is not accompanied by ionisation of the argon, but at 15·1 volts ionisation of the argon takes place. The latter potential corresponds, according to the quantum relation, with a wave-length of 817 Å.U., which is in accord with the spectroscopic investigation of the extreme ultraviolet spectrum of argon by Lyman, which he found terminated abruptly at 800° Å.U. Evidence has been obtained that at 15·1 volts not all the collisions are fruitful in producing ionisation, and that the fraction of fruitful collisions is increased greatly by intense 11·5 volt radiation. The minimum ionisation velocity, 15·1 volts, however, is the same whether the argon is exposed to weak or intense 11·5 volt radiation. F. S.

Investigation of the Effects of Electron Collisions with Platinum and with Hydrogen, to ascertain whether the Production of Ionisation from Platinum is due to Occluded Hydrogen. FRANK HORTON and ANN CATHERINE DAVIES (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 23—43).—During the investigation of electron collisions with helium it was found that positive ions were produced from a positively charged platinum gauze bombarded with electrons of minimum velocity corresponding with 11 volts, and this has been more fully investigated to determine whether it is due to the metal or to attached hydrogen. This voltage is subject to a correction for the velocity at which the electrons leave the tungsten filament, and the mean of all the corrected results gives 13·0 volts as the critical electron velocity for the production of the ionisation, which does not agree with the usually accepted value of the "ionisation potential" of hydrogen (11 volts). In the same apparatus the production of ionisation in hydrogen was investigated, hydrogen being introduced through a palladium tube heated in a flame, and the conclusion was reached that the first critical velocity (13 volts) is not due to hydrogen at all, but probably

to the platinum itself. In hydrogen it was found that a radiation is produced at an electron velocity of 10·5 volts, a second type of radiation at 13·9 volts, an ionisation at 14·4 volts, and a second type of ionisation at 16·9 volts. These four velocities correspond probably with radiation from the hydrogen atom and molecule and ionisation of the hydrogen atom and molecule respectively, the values calculated from Bohr's theory being 10·2 instead of 10·5 for the first, 13·6 instead of 14·4 for the third, and 16·3 instead of 16·9 for the fourth. It is desirable that these critical velocities be further examined in an apparatus specially designed for the purpose. F. S.

Melting Point of Lead Isotopes. M. E. LEMBERT (*Zeitsch. Elektrochem.*, 1920, **26**, 59—60).—The melting points of pure lead chloride and lead chloride containing Ra-*G* chloride have been determined and shown to agree to within 0·06%, that is, to within 0·5°. The material used for the determination was that used by Richards and Lembert for atomic-weight determinations, and from which the values 207·15 and 206·57 respectively were obtained (A., 1914, ii, 683). The present results confirm the assumption of Fajans (A., 1915, ii, 206) that v^2m is constant for isotopes as against the view of Lindemann (*Nature*, 1915, **95**, 7) that v is constant. J. F. S.

The Radioactivity of Bavarian Rocks and Waters and of the Fluorspar of Wölsenberg. F. HENRICH (*Zeitsch. angew. Chem.*, 1920, **33**, 5—8, 13—14, 20—22).—An investigation of the distribution of radioactivity in the springs, rocks, and minerals of Bavaria, including also French Switzerland, the Fichtelgebirge, and the Oberpfalz, is described with details of the activity of a large number of springs expressed in Mache units (*M.U.*). The springs in the chalk mountains of French Switzerland were but feebly active, but in the granitic areas of the Fichtelgebirge most of the springs had an activity between 10 and 100 *M.U.* and four were over 100 *M.U.* The minerals tobernite and autunite occurred in these districts in the granite. A special examination of the gases from one of the springs showed the unusual composition of about 12% of oxygen and the rest "unabsorbable."

A description is given of the fluorspar of Wölsenberg ("Stinkfluss"), in which the dark blue and violet-coloured varieties emit a peculiar odour on being crushed, which is undoubtedly due to the evolution of free fluorine. The origin of this is considered to be due to the action of rays of radioactive substances, dissociating the calcium fluoride, with coloration of the mineral due to colloidal calcium and evolution of free fluorine. By acting on fluorspar with radium rays the colour is easily produced, but not the odour of fluorine. F. S.

Dependence of the Dielectric Constants of Water, Ethyl Alcohol, Methyl Alcohol, and Acetone on Pressure. G. FALCKENBERG (*Ann. Physik*, 1920, [iv], **61**, 145—166).—The dielec-

tric constant of water, ethyl alcohol, methyl alcohol, and acetone has been determined at temperatures (16·3—20°) over the pressure range 7—200 atms. The mean change in the dielectric constant per atmosphere increase in pressure is found to be 0·0046% for water, 0·0097% for ethyl alcohol, 0·0102% for methyl alcohol, and 0·016% for acetone. The refraction constants $(n-1)/d$, $(n^2-1)/d$, and $(n^2-1)/(n^2+2) \cdot 1/d$ are calculated for the above-named liquids at the pressures named. In the case of water and both alcohols a good agreement is found for the expression $(n^2-1)/d$, both at low and high pressures. In the case of acetone, owing to insufficient knowledge of the compressibility, conclusions are not arrived at. Using the results of Ortvay (A., 1911, ii, 961), the values of $(n^2-1)/d$ and $(n-1)/d$ are calculated for benzene and ethyl alcohol. In the case of benzene the value of $(n^2-1)/d$ is constant over the range 1—500 atmospheres; but with ethyl alcohol all three values show considerable irregularity over the same pressure range. The very large values of the Wiener number u for water and the two alcohols confirm the suggestion of Röntgen that the ratio of polymerised to non-polymerised molecules changes with increase of pressure. J. F. S.

[Electrical] Conductivity of Solid Salts and Mixtures of Salts. ROBERT KETZER (*Zeitsch. Elektrochem.*, 1920, **26**, 77—84).—The specific conductivity of pastilles of lead chloride, lead bromide, and mixtures of these substances with varying amounts of sodium and potassium chloride and bromide respectively has been determined at 37°. Electrical contacts were made with amalgamated copper plates, and it is shown that differences in conductivity amounting to 12% may be occasioned by variations in the pressure employed in making the pastille. It is shown that the large increase in conductivity found by Fritsch (A., 1897, ii, 301) on mixing the haloids of lead and mercury with alkali haloids, does not occur if moisture is completely removed and if the mixture is not heated to a high temperature. It is shown that the previous treatment of lead chloride has a marked influence on the conductivity. In the case of the mixtures, it is found that heating before pressing increases the conductivity to a considerable extent. Thus 2% of sodium chloride in lead chloride increases the conductivity of the lead chloride 109—170 times, if the previous heating was carried out in moist air, in a vacuum, or in chlorine; on heating in dry air the increase was 41 times. The very smallest additions to lead chloride produced a considerable increase in conductivity; thus, 0·001% of sodium chloride increased the conductivity 45 times if the mixture was melted in chlorine before pressing. No proportionality was found between the concentration of the alkali chloride and the increase in conductivity. J. F. S.

Form of the Conductivity Function in Dilute Solutions. CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1920, **42**, 1—18).—A theoretical paper, in which the method adopted by Washburn (A., 1918, ii, 55) for calculation of the value of k, is examined

The author is not able to agree either with Washburn's conclusions or with his interpretation as to the limiting character of the law of mass action. J. F. S.

Conductivity and Viscosity of Organic and Inorganic Salts in Formamide and in Mixtures of Formamide with Ethyl Alcohol. P. B. Davis and H. I. Johnson (*Carnegie Inst. Pub.*, 1918, **260**, 71—96).—The conductivity and the viscosity in formamide solution of (*a*) metallic nitrates and formates (common anion), and (*b*) sodium salts of organic acids (common cation) have been measured, and also the behaviour of certain representative salts in mixtures of formamide and ethyl alcohol has been studied. The molecular conductivities of ammonium, potassium, sodium, calcium, strontium, and barium nitrates in formamide, which has a greater dissociating power than water, are much smaller than in aqueous solution. Evidence of complex solvent formation is obtained with the calcium, strontium, and barium salts in formamide and in water. From the conductivities and viscosities of the formates of rubidium, ammonium, lithium, sodium, barium, and strontium in formamide at 15°, 25°, and 35°, the conclusions are drawn that these salts, like the nitrates, are more strongly dissociated at low dilutions in formamide than in water, that the temperature-coefficients of the conductivities are of the same order of magnitude for the alkali formates, but are greater for the alkaline-earth formates, and that rubidium and ammonium formates increase the viscosity less than sodium and lithium formates.

From conductivity and viscosity measurements in formamide at 15°, 25°, and 35° of sodium *m*-bromo-, *m*-amino-, and 3 : 5-dinitrobenzoate, benzoate, salicylate, benzenesulphonate, and succinate, the conclusions are drawn that (*a*) the conducting capacity of the first three salts is approximately the same, and the same is true of the next three. All monobasic salts have nearly the same conductance, which is about half that of the dibasic salt; (*b*) no relation exists between the conductivity and the constitution of the organic salts, and the same is true of the viscosity.

Data were also obtained on the molecular conductivity and the viscosity of tetramethylammonium iodide, rubidium iodide, lithium nitrate, and calcium nitrate in mixtures of formamide and ethyl alcohol. The first three salts show an increase in molecular conductivity up to a concentration of 25% formamide and 75% ethyl alcohol, where a maximum is reached, a fact explicable by an increase of ionic mobility at this point. Cæsium, rubidium, and potassium salts lower the viscosity of water, but increase that of formamide. Chemical Abstracts.

Electrical Conductivity of the Sodium Salts of certain Organic Acids in Absolute Alcohol at 15°, 25°, and 35°. H. H. Lloyd and A. M. Pardee (*Carnegie Inst. Pub.*, 1918, **260**, 99—118).—An extension of previous work on the electrical conductivity and dissociation of various organic acids in alcoholic solu-

tion, involving a study of the sodium salts of the organic acids in absolute alcoholic solution to obtain first the λ_0 values for these salts and then the λ_0 values for the acids. Absolute alcoholic solutions of thirty-two sodium salts were prepared, and the conductivities at 15°, 25°, and 35° over the range $N/50$ to $N/20,000$ were determined. Goldschmidt's previous results were confirmed. The λ_0 values were obtained by extrapolation, using the function $1/\lambda = 1/\lambda_0 + K(C\lambda)^{n-1}$ developed by Noyes and Johnston. The Kohlrausch formula did not give satisfactory results. The λ_0 values at 25° were obtained for all the salts, and by combination with the λ_0 values for hydrogen and sodium chlorides the limiting conductivity at 25° of thirty-one organic acids in absolute alcoholic solution was calculated. The dissociation and affinity constants of these acids in such solution can be calculated from the λ_0 values. There is a great similarity in the conductivity of these organic acids in alcohol. Little can be said of the relation between chemical composition and conductivity. No difference was found between aliphatic and aromatic derivatives, and the position of substituents in the latter appeared to be without influence on the conductivity. CHEMICAL ABSTRACTS.

The Positive Influence which the αγ-Diols Exercise on the Conductivity of Boric Acid. J. BÖESEKEN (*Rec. trav. chim.*, 1920, **39**, 178—182).—[With W. ROST VAN TONNINGEN.]—Diethylmalonic acid has $K_{25} = 2{\cdot}8 \times 10^{-8}$, and is notably much stronger than diglycollic acid (compare A., 1916, ii, 595). It might be expected, therefore, to have a feebler negative influence on the conductivity of boric acid, but the diminution found is almost the same in the two cases.

[With W. F. Th. HENDRIKSZ.]—Measurements with β-nitro-β-methylpropane-αγ-diol give results almost equal to those of glycerol and much less than those of pentaerythritol. W. G.

The *cyclo*Hexane-1 : 2-diols and the Flexibility of the Benzene Ring. J. BÖESEKEN and J. VAN GIFFEN (*Rec. trav. chim.*, 1920, **39**, 183—186).—Measurements have been made with the *cis*- and *trans*-*cyclo*hexane-1 : 2-diols to determine their influence on the conductivity of boric acid. The influence of both isomerides is manifestly negative, but the influence of the *cis*-isomeride is slightly more feeble than that of the *trans*-isomeride. The *cis*-diol shows a greater tendency to form complexes than the *trans*-diol. The authors explain the difference of behaviour of these two isomerides on the hypothesis that the flexibility of the *cyclo*hexane ring permits of the hydroxyl groups of the *cis*-form obeying more easily their natural repulsion. W. G.

Increase in the Conductivity of the α-Keto-acids by Boric Acid, as a Consequence of the Formation of α-Hydroxy-acids by Hydration: $R{\cdot}C(OH)_2{\cdot}CO_2H$. J. BÖESEKEN and W. ROST VAN TONNINGEN (*Rec. trav. chim.*, 1920, **39**, 187—190).—Trimethylpyruvic acid, like pyruvic acid itself (compare A., 1916,

ii, 209), exerts a marked positive influence on the conductivity of boric acid itself, thus confirming the view previously expressed (*loc. cit.*) that the α-keto-acids in aqueous solutions are hydrated and behave like dihydroxy-compounds. Trimethylpyruvic acid is notably much weaker than pyruvic acid, and the dehydration takes place more easily, so that it apparently exerts a negative influence even at moderate dilutions. W. G.

Overpotential and Catalytic Activity. ERIC K. RIDEAL (*J. Amer. Chem. Soc.*, 1920, **42**, 94—105).—The influence of temperature on overpotential has been determined at a series of temperatures for platinum, copper, and zinc. In the case of zinc, there is no relationship between the calculated and observed temperature-coefficient, the latter only amounting to 0·31 millivolt per degree at 37°. In the case of copper and platinum, a higher coefficient is observed, the values being 2·2 millivolts per degree and 0·17 millivolt per degree respectively. These values are three to four times as large as the calculated values. It is suggested that overpotential is a measure of the energy required for the desorption of hydrogen from a metal surface. Metals with low latent heats of desorption are catalytically active, the activity increasing with decreasing overpotentials. Metals with overpotentials exceeding 0·455 volt are catalytically inert, and no metal can posess an overvoltage exceeding 1·80 volts. The calculated values of the catalytic activities of the metals are in agreement with Sabatier's qualitative observations. A suggestion is made for the mechanism of the process of desorption on the radiation hypothesis. J. F. S.

Resemblances between the Properties of Surface Films in Passive Metals and in Living Protoplasm. II. RALPH S. LILLIE (*Science*, 1919, **50**, 416—421. Compare A., 1919, i, 606).—Most ions activate passive iron at varying rates and the stability of the surface film in any solution, and hence the preservation of the passive state, is dependent on the oxidising properties of the dissolved substance. Continued oxidation seems to be necessary for preservation of passivity. Ions of strong oxidising properties tend to stabilise regardless of charge, for example, the dichromate, permanganate, silver, gold, and platinum ions. The haloid ions have a *strong activating influence, the rate being proportional to the* concentration. Salts with terminal oxygen in union activate only very slowly. The cation has not so large an effect, but passivity is retained longer in solutions of heavy metal salts. Any condition that confers increased stability on the surface film prevents or retards its destruction in an activating solution. Hence oxidising anions or cations more noble than the experimental metal antagonise the activating effects of other ions. The antagonism between sodium and calcium so characteristic in biological systems is not exhibited by passive iron. Anæsthetics, except ethyl nitrate, show no retarding effect towards activation as they do in protoplasm, but

this is not to be expected since solution in the organic solvents of the protoplasm, particularly lipoids, is not paralleled by any process of solution in the metals. CHEMICAL ABSTRACTS.

Simple Hydrogen Electrode. C. H. BAILEY (*J. Amer. Chem. Soc.*, 1920, **42**, 45—48).—The vessel and electrode for preparing a simple hydrogen cell may be constructed as follows. A piece of 7 mm. bore tube is blown out at one end to form a bulb 15 mm. diam.; the tube is then bent to form an angle of about 45° at a distance of 50 mm. from the top of the bulb. The other limb of the tube is about 80 mm. long, and is fitted with a ground-glass stopper. The metal electrode is a thin gold disk 5 mm. diam. welded to a piece of thin platinum wire and fused into the side of the shorter limb of the tube about 5 mm. above the bend. The gold foil is platinised in the usual way. The tube is filled with the liquid under investigation, and then by means of a fine tube the bulb is filled with pure hydrogen, thus expelling some of the liquid. It is then stoppered, care being taken to exclude all air, and vigorously shaken until the solution is saturated with hydrogen. Connexion is made with the standard electrode by removing the stopper and placing the syphon tube well down the longer limb. The electrode is stated to give trustworthy results, and to be very rapid in its action. J. F. S.

A Gas Collecting Tube. ERICH MÜLLER (*Zeitsch. Elektrochem.*, 1920, **26**, 76—77).—A gas burette for collecting the gases evolved at electrodes during electrolysis is described. The novelty of the apparatus lies in the tap which is attached at the bottom of the burette; this is a heavy tap with a key bored in T-shape, so that the horizontal bore will give access to the burette and the vertical bore to a side-tube to which the levelling tube is attached.
J. F. S.

New Cadmium Vapour Arc Lamp. FREDERICK BATES (*Phil. Mag.*, 1920, [vi], **39**, 353—358).—A small quartz cadmium vapour lamp is described. The lamp is in the form of an inverted U-tube of 10 c.c. capacity, and is fitted with two long quartz capillaries at its ends, by means of which the tungsten wire electrodes are admitted. The electrodes are fastened into the capillaries by means of lead seals. The lamp is filled by distilling, from a quartz bulb attached at the bend of the U-tube, a gallium–cadmium alloy containing 2—3% of gallium. The presence of the gallium renders the cadmium soft, and so prevents breakage of the lamp when the metal solidifies. The distillation is carried out at 0·001 mm. pressure, and when sufficient has been distilled into the lamp the narrow tube by which the bulb is connected is sealed. The lamp will burn with 110 volts and 3 amperes with a drop of 14 volts across the terminals, but is more efficient with a current of 7 amperes and a drop of 25 volts. To start the lamp one limb must be heated with a bunsen flame. The spectrum of the light thus produced is prac-

tically that of pure cadmium; the lamp is durable, and requires little attention, and furnishes an intense monochromatic source of red light by means of the line λ 6439 Å. J. F. S.

Magnetic Susceptibilities of Hydrogen and some other Gases. TAKÉ SONÉ (*Phil. Mag.*, 1920, [vi], **39**, 305—350, and *Sci. Rep. Tohoku. Imp. Univ.*, 1919, **8**, 115—167).—The magnetic susceptibility of air, oxygen, carbon dioxide, atmospheric nitrogen, chemically pure nitrogen, argon, and hydrogen has been determined with reference to water $= -0.720 \times 10^{-6}$. The following specific susceptibilities ($\chi\, 10^6$) at 20°, and volume susceptibilities ($\kappa\, .\, 10^6$) at 0° and 760 mm. are found: air, $\chi = 23.85$, $\kappa = 0.03084$; oxygen, $\chi = 104.1$, $\kappa = 0.1488$; carbon dioxide, $\chi = -0.423$, $\kappa = -0.000836$; chemically pure nitrogen, $\chi = -0.265$, $\kappa = -0.000331$; atmospheric nitrogen, $\chi = -0.360$, $\kappa = -0.000452$; argon, $\chi = -5.86$, $\kappa = 0.0104$; hydrogen, $\chi = -1.982$, $\kappa = -0.0001781$. The susceptibility of air as determined is very close to that calculated from the values for the constituent gases, which indicates that the additive rule holds for the susceptibility of gases. The susceptibility of nitrogen is found to be diamagnetic, a fact which is opposed to the values of all other observers except Pascal, who found it had a value about 50% greater than the present value. The specific susceptibilities of gaseous and solid carbon dioxide have the same value. The present results are considered in the light of Bohr's atomic model for hydrogen. J. F. S.

Moment of Inertia of the Magneton. R. GANS (*Ann. Physik*, 1920, [iv], **61**, 396—397).—A theoretical paper, in which the moment of inertia of the magneton of a number of elements is calculated. This value is of the same order in most cases, and lies between 0.761×10^{-43} and 60.2×10^{-43}. The moment of inertia of platinum is 67.7×10^{-40} and of anhydrous manganous sulphate 12.4×10^{-40}. J. F. S.

Magneto-chemistry of the Chromic Chlorides. JOSÉ BALTÁ ELIAS (*Anal. Fís. Quím.*, 1918, **16**, 467—483).—The magnetic susceptibility of aqueous solutions of the green and the violet chromic chloride was determined at different degrees of concentration, temperature and acidity, and during transformation of either modification into the other. Quincke's method was employed for dilute, and the solenoid method for concentrated, solutions. The susceptibility of the solutions of either salt was found to be independent of the concentration, hence they comply with Wiedemann's law (that is, the susceptibility is an additive property, obtained as the sum of those of its components). The conversion of the green into the violet solution and vice versa was not marked by any change in the magnetic constant within the intervals in which the measurements were made (up to eight hundred and eighty-six hours). Hence the two modifications have the same magnetic constant, whereas their

other physical properties are different. It is inferred that—unlike cobalt, the magnetic properties of which undergo profound changes in certain co-ordination compounds—the linking between chromium and the other atoms or radicles in its co-ordination sphere is effected through the more external electronic orbits of the atom. The existence of nineteen magnetons in the chromium atom is confirmed (compare Cabrera and Marquina, A., 1917, ii. 355). The magnetic constant of both salts decreases in dilute solutions, but in presence of hydrochloric acid hydrolysis is repressed and the (stable) green chloride regenerated. The figures obtained for the molecular susceptibilities ($\gamma^{(M)}$) of the two compounds are given below, together with those obtained by Feytis (A., 1913, ii, 381):

	Elias.	Feytis.
$[Cr(H_2O)_6]Cl_3$	6181.10^{-6}	5920.10^{-6}
$[CrCl_2(H_2O)_4]Cl.2H_2O$ ...	6179.10^{-6}	6100.10^{-6}

W. R. S.

Establishing of the Absolute Temperature Scale. Frederick G. Keyes (*J. Amer. Chem. Soc.*, 1920, **42**, 54—59).—A theoretical paper, in which the work of Buckingham and of Chappuis on the absolute temperature scale is considered from the point of view of the author's new equation of state, which is based on the Bohr conception of the atom (*Proc. Nat. Acad. Sci.*, 1917, **3**, 323). J. F. S.

Characteristics of the Gouy Thermo-regulator. T. S. Sligh, jun. (*J. Amer. Chem. Soc.*, 1920, **42**, 60—68).—The paper describes a modification of the usual type of electrical thermo-regulator in which the fixed contact element is replaced by an oscillating contact element, and shows that such a regulator will reduce the periodic variations of the bath temperature and the erratic variations due to variations of the mercury surface to a fraction of the values obtainable with the usual form of thermo-regulator. A periodic variation in bath temperature of less than 0·0001°, as indicated by a temperature indicator, having a natural period of about five seconds is easily obtained. By the use of an oscillating contact regulator, variations of mean bath temperature due to variations in external conditions are reduced below the values usually obtained. Characteristic equations are derived for both the fixed and oscillating type of thermo-regulator, and these equations, together with experimental data, have been used to draw a comparison between the two types of regulator. J. F. S.

Variation of Thermal Conductivity during the Fusion of Metals. Seibei Konno (*Sci. Rep. Tohoku. Imp. Univ.*, 1919, **8**, 169—179).—The thermal conductivity has been determined for tin (18—498°), lead (18—601°), bismuth (18—584°), zinc (18—578°), aluminium (18—800°), and antimony (0—692°). The thermal conductivity of tin, lead, zinc, and aluminium decreases with rise of temperature up to the melting point. On melting the thermal

conductivity of these metals decreases abruptly and to a considerable extent. The thermal conductivity of bismuth and antimony decreases to a minimum, which lies at 160° and 182° respectively, and then slowly rises to the melting point. On melting the thermal conductivity of bismuth increases considerably, whilst that of antimony appears to decrease slightly. The thermal conductivity of the molten metals in all cases decreases slightly with increase in temperature. The changes in thermal conductivity run parallel with the changes in electrical conductivity with rise in temperature. J. F. S.

***Variation of Atomic Heats as a Function of the* Temperature.** MATHEUS D'A. ALBUQUERQUE (Pamphlet [Portuguese], 1919, 1—19).—A theoretical discussion.

Melting Points of Pure Metals. W. GUERTLER and M. PIRANI (*Zeitsch. Metallkunde*, **11**, 1—7; from *Chem. Zentr.*, 1919, iii, 910—911).—The following are given as the most trustworthy figures for the melting points of the elements: Ag, 961°; Al, 658°; As, 850° (?); Au, 1063°; B, 2400°; Ba, 850°; Gl, 1300° (?); Bi, 270°; C, >3600°; Ca, 809°; Cd, 321°; Ce, 700°; Cl, −101·5°; Co, 1490°; Cr, 1520°; Cs, 26°; Cu, 1084°; Fe, 1530°; F, −223°; Ga, 30°; Ge, 958°; H, −259°; Hg, −39·7°; I, 113·5°; In, 155°; Ir, 2350°; K, 62·4°; La, 810°; Li, 186°; Mg, 651°; Mn, 1210°; Mo, 2410° (?); N, −210°; Na, 97·5°; Cb, 1700° (?); Nd, 840°; Ni, 1452°; O, −218°; Os, 2700° (?); P, 930°; Pb, 327·4°; Pd, 1545°; Pr, 940° (?); Pt, 1760°; Ra, 700°; Rb, 38°; Rh, 1960°; Ru, 2450° (?); S, 119·2°; Sa, 1300°; Sb, 630°; Se, 217°; Si, 1420°; Sr<Ca<Ba; Sn, 232°; Ta, 2800°; Te, 450°; Th>Pt, 1800°; Ti, 2000° (?); Tl, 301°; U, >1850°; V, 1800°; W, 3030°; Y, 1490°; Zn, 419·4°; Zr, 1700° (?).

The dependence of the melting point on the position of the element in the periodic system is also graphically illustrated. H. W.

Thickness of the Capillary Layer between the Homogeneous Liquid and Vapour Phases, particularly for Carbon Dioxide. G. BAKKER (*Ann. Physik*, 1920, [iv], **61**, 273—302. Compare A., 1919, ii, 12; this vol., ii, 19).—A theoretical paper, in which the thermodynamic equation $(E_1-E_2)/2-E_3=T^2\{d(H/\zeta T)/dt\}$ is deduced by two methods: H is the surface tension, ζ the thickness of the capillary layer, T the absolute temperature, and E_1, E_2, and E_3 are the energy densities (energy per unit volume) of the liquid, vapour, and unstable phases respectively. The thermodynamic potential of the unstable phase has the same value as the homogeneous liquid and vapour phases. Making use of the formulæ of Gauss—van der Waals and Mills, the following thicknesses are calculated for the capillary layer of carbon dioxide: −25°, 1·52 μμ; −10°, 1·51 μμ; 0°, 1·87 μμ; 10°, 2·13 μμ; 20°, 3·11 μμ; 28°, 5·86 μμ; 30°, 13·66 μμ; and 31·12°, 193 μμ. Mak-

ing use of a different method of calculation, the values for the number of layers in the capillary layer R and the total number of layers n of gas and liquid which form the capillary layer are calculated. For carbon dioxide the values are:

t =	−25°,	−10°,	0°,	10°,	20°,	28°.
R =	3·0	3·6	4·2	5·1	7·0	11·4
n =	2·7	3·4	4·0	4·9	6·9	11·3
ζ =	1·6	2·0	2·3	2·8	3·2	6·1 $\mu\mu$.

The value of R has also been calculated for benzene and ether. These are based on the van der Waals's equation of state, and are as follows: (1) benzene, 5·4°, 2·4; 50°, 3; 100°, 3·4; 150°, 3·5; 200°, 4·0; 250°, 10·8; and 280°, 16; (2) ether, 0°, 2·4; 20°, 3·3; 50°, 3·3; 80°, 4·2; 120°, 5; 170°, 7·8; 190°, 16·4; and 193°, 21·5. J. F. S.

Certain Binary and Ternary Mixtures of Liquids having Constant Boiling Points. WILLIAM RINGROSE GELSTON ATKINS (T., 1920, **117**, 218—220).

Brown's Formula for Distillation. SYDNEY YOUNG (*Sci. Proc. Roy. Dubl. Soc.*, 1920, **15**, 667—672).—Brown's formula, $M'_A/M'_B = c \cdot M_A/M_B$ (where M'_A, M'_B, and M_A, M_B are the relative number of molecules of A and B in the vapour and liquid phase respectively, and c is a constant depending on the relative vapour pressures of the pure substances at the boiling point of the mixture), is applicable without serious error to mixtures of benzene and toluene, of which the vapour pressure P approximately equals $MP_A + (1-M)P_B$, P_A and P_B being the vapour pressures of the two pure substances at the same temperature, and M the molar fraction of the substance A. Further, for benzene and toluene the best value of the constant c differs but slightly from the ratio P_A/P_B, namely, 2·591. G. F. M.

Thermodynamics and Probability. A. BERTHOUD (*J. Chim. Phys.*, 1919, **17**, 589—624).—A mathematical discussion of the relationship between entropy and probability, in which a formula is given by means of which it is possible (1) to determine the most probable distribution of the molecules of a monatomic or diatomic gas, according to their velocity or energy, this distribution being expressed by the generalised Maxwell formula; (2) to find the relationship which expresses the *entropy* of a *monatomic* or diatomic gas in terms of its temperature and its volume, this relationship agreeing with the thermodynamic expression of entropy. W. G.

Free Energy and the Hypothesis of Nernst. A. BOUTARIC (*Le Radium*, 1919, **11**, 257—262, 298—305, 348—356).—The author directs attention to the well-known looseness of terminology of writers on the free energy equation, $A - U = T(dA/dT)$. He deduces

this, and numerous other equations, by familiar methods, and considers their application to some special examples. J. R. P.

Heats of Dilution of Certain Aqueous Salt Solutions. ALLEN EDWIN STEARN and G. McP. SMITH (*J. Amer. Chem. Soc.*, 1920, **42**, 18—32).—The reversible molecular heat of dilution has been determined for the chlorides of sodium, potassium, and strontium at various concentrations ranging from 3·2 weight N to 0·2 weight N, and also for solutions of mixtures of pairs of the abovenamed salts in equivalent and molecular quantities. The heats of dilution of sodium and potassium chlorides are negative. This fact in the light of the equation $L_D = RT^2 . (d \log_e p/p_0)/dT$, in which L_D is the molecular heat of dilution, indicates an increase in the degree of ionisation with temperature, which is contrary to the experimental results of Noyes (A., 1912, ii, 526), unless they are explained on the basis of decomposition of complexes which exist in solution, but are decomposed on dilution. The heats of dilution for the solutions of mixed salts bear no simple additive relation to the heat effects of the single components at equivalent concentrations. The results are explained on the basis of higher order compounds as put forward by Werner. J. F. S.

Heats of Dilution of Solutions of Barium Chloride and Barium-Sodium Chloride Mixture. G. McP. SMITH, ALLEN E. STEARN, and R. F. SCHNEIDER (*J. Amer. Chem. Soc.*, 1920, **42**, 32—36. Compare preceding abstract).—The reversible molecular heat of dilution has been determined for solutions of barium chloride of 3·2, 2·8, and 1·6 weight N, and for solutions of the mixed salts in equivalent proportions of 3·2, 1·6, 0·8, and 0·4 weight N. It is shown that the heat of dilution of the mixture of salts bears no simple additive relationship to the heat of dilution of the components at equivalent dilutions. The behaviour of barium chloride in this respect is therefore analogous to that of strontium chloride (*loc. cit.*). The experimental results can be explained on the same basis as the results obtained with the mixed strontium salts, namely, on the assumption of the formation of compounds of a higher order. J. F. S.

Relations between Relative Densities, Absolute Density, and Apparent Weight of Solutions. O. CHÉNEAU (*Bull. Assoc. Chim. Sucr.*, 1919, **37**, 175—181).—For the interconversion of specific gravity results at 15°, from one basis of reference to another, a table has been compiled showing absolute densities (that is, 15° in vacuum/water at 4° in vacuum), and, in parallel columns, the corrections to be added or subtracted to arrive at corresponding values referred to any of the following bases: 15° in air/water at 15° in air, 15° in vacuum/water at 15° in vacuum, 15° in vacuum/water at 15·5° in vacuum, and 15° in air/water at 4° in vacuum. The values are given to five places of decimals, and range from 0·7 to 1·8. J. H. L.

Investigation of Mewes' Law of the Relation between the Volume of a Gas and the Temperature. RUDOLF MEWES (*Zeitsch. Sauerstoff. Stickstoff. Ind.*, 1919, **11**, 73—75, 91—93; from *Chem. Zentr.*, 1920, i, 104, 278. Compare Mewes and Neumann, A., 1919, ii, 493).—(*a*) The errors observed in the previous experiments are to be ascribed, in part, to the presence of impurities and consequent liquefaction.

In the second paper the author shows that Landolt's expression, $(n_{tp}-1):(n_{0\cdot 760}-1)=d_{tp}$, is valid for low temperatures if errors due to partial condensation of the gas by surface action and partial liquefaction are eliminated. H. W.

Electrical Nature of the Cohesive Forces of Solid Substances. M. BORN (*Ann. Physik*, 1920, [iv], **61**, 87—106).—A mathematical paper in which relationships are deduced for the molecular forces existing in crystals of the alkali haloids. It was shown by Born and Landé (A., 1919, ii, 188) that the compressibility of these salts can be explained by the assumption that the ions exercise attractive and repulsive forces on one another in the sense of Coulomb's law, and that two ions exercise a repulsive force the potential of which is inversely proportional to the ninth power of the distance between the ions. The present calculations are based on this assumption. J. F. S.

Surface Tension of Mixtures of Water and Alcohol. JAMES BRIERLEY FIRTH (T., 1920, **117**, 268—271).

The Adhesion of Starch at Fluid Surfaces. I. Experiments with Starch Grains. F. B. HOFMANN (*Pflüger's Archiv*, 1917, **167**, 267—279; from *Physiol. Abstr.*, 1917, **2**, 541).—Potato-starch has been used to study the adhesion of solids when distributed between two immiscible liquids, and the conditions which influence this adhesion. J. C. D.

The Viscosity of Cæsium Salts in Glycerol-Water Mixtures. P. B. DAVIS (*Carnegie Inst. Pub.*, 1918, **260**, 97—98).—An extension of previous studies by Jones and others on the viscosity of solutions in glycerol and in binary mixtures containing glycerol, with special reference to those salts known to decrease the viscosity of water and of glycerol. Rubidium and cæsium iodides produced phenomenal lowering of the viscosity of glycerol. In these experiments the viscosities of cæsium nitrate and cæsium chloride were measured at 25° and 35°. Cæsium salts decrease the viscosity of glycerol–water mixtures more than rubidium salts. When salts of both rubidium and cæsium increase the solvent viscosity, as, for example, water and acetone or water and the alcohols, the cæsium salt produces a smaller increment than the rubidium salt. CHEMICAL ABSTRACTS.

The Sorption of Hydrogen by Palladium at Low Temperatures. JAMES BRIERLEY FIRTH (T., 1920, **117**, 171—183).

The Effect of Heating on the Absorptive Power of Sugar-charcoal for Sulphur Dioxide. RAMSAY MIDDLETON WINTER and HERBERT BRERETON BAKER (T., 1920, **117**, 319—321).

Influence of Temperature on the Adsorbability, the Colloid-precipitating Power of some Narcotics. R. BIERICH (*Pflüger's Archiv*, 1919, **174**, 202—217; from *Physiol. Abstr.*, 1919, **4**, 184).—The observation of Meyer and Overton of the partition-coefficients between oil and water was confirmed for the partition between cod-liver oil and water in the case of salicylamide and benzamide. The adsorption of narcotics by animal charcoal was found to be almost unaffected by alteration of temperature. In the investigation of the colloid-precipitating power it was found that with *iso*butyl alcohol, ethylurethane, propylurethane, benzamide, and salicylamide the precipitation of serum albumin by cobalt chloride is strengthened more at high than at low temperatures; the same applied for some of the narcotics with the sodium chloride precipitation of colloidal ferric hydroxide. The narcotic power as tested on tadpoles was always increased by rise of temperature. As regards benzamide and salicylamide this is opposed to the observation of Meyer that the threshold strength of the narcotic varies in the opposite direction to the oil–water partition-coefficient. J. C. D.

Adsorption by Precipitates. II. HARRY B. WEISER and EDMUND B. MIDDLETON (*J. Physical Chem.*, 1920, **24**, 30—73. Compare A., 1919, ii, 269).—The amount of adsorption of phosphate, citrate, tartrate, oxalate, sulphate, iodate, and dichromate ions by definite quantities of precipitated ferric oxide from a ferric oxide sol has been determined. It is shown that since the first process in the precipitation of a colloid by an electrolyte is the *neutralisation of the charge by the adsorption of an ion of opposite charge*, it follows that two adsorbing media are concerned in the process: the electrically charged particles and the electrically neutral particles. Accordingly, the total amount of a given ion carried down by a precipitated colloid is determined by (*a*) the adsorption by the electrically charged particles during the process of neutralisation, and (*b*) the adsorption of the electrically neutral particles during the process of agglomeration and settling. The failure to take the second cause into consideration has led to the erroneous conclusion that the amounts of all precipitating ions carried down by a precipitated colloid are equivalent. The adsorption *of equivalent amounts of precipitating ions will neutralise a* given amount of colloid, provided the stabilising effect of the ion *having the same charge as the colloid is kept constant*; but the amounts adsorbed by the neutralised particles will vary with the nature of the adsorbing medium, the nature of the adsorbed ion, and the concentration of the ion in the solution. The determination of adsorption values at the precipitation concentration, as a rule, will not give comparable results because of the variability in

the latter, and the consequent variability in the degree of saturation of the adsorbent in the adsorbed phase. The variations from strict equivalence in the adsorption values of Freundlich are probably due quite as much to the varying concentration and adsorbability of the ions as to the analytical errors. The ions mentioned above are strongly adsorbed by hydrated ferric oxide. The adsorption of univalent ions was relatively weak, so that the precipitate was readily peptised by washing. The amounts of the ions adsorbed are not even approximately equivalent. The phosphate on is most strongly adsorbed, and the others follow the order: phosphate>citrate>tartrate > oxalate > sulphate > iodate > dichromate. The order of adsorption determined by analysis is ntirely different from the order deduced from precipitation values on the assumption that the most strongly adsorbed ion precipiates in the lowest concentration. The latter order is: dichromate> artrate>sulphate>citrate>oxalate>iodate>phosphate. In addiion to the effect of the valency and the adsorbability of precipiating ions, the precipitating values are influenced by differences in he degree of ionisation of electrolytes, the hydrolysis of certain alts, the stabilising effect of the ion having the same charge as the olloid, the mobility of the ions which in certain cases decreases with dilution owing to increased hydration, the rate of coagulation, nd the method of determining the critical concentrations. The rder of precipitation values is the same for the acids as for their otassium salts except that the former precipitate in somewhat igher concentration than the latter owing to the stabilising effect f the strongly adsorbed hydrogen ion. There is apparently no onnexion between the precipitation values and the ionisation onstants of the acids investigated, probably because precipitation akes place at such small concentrations (0·0002—0·0008N). The rder of precipitation values of the potassium salts is: ferroyanide<ferricyanide<dichromate<tartrate < sulphate < oxalate <chromate<iodate<bromate < thiocyanate < chloride < chlorate <nitrate<bromide<iodide<formate. There is a tendency for ions f the highest valency to be most strongly adsorbed. That there re exceptions to this rule and that ions of the same valency are requently adsorbed in widely varying amounts may be expected, nce adsorbability is a specific property of the ions. J. F. S.

Attempt to Extend Planck's Theory of Dilute Solutions. . BOEDKE (*Ann. Physik*, 1920, [iv], **61**, 334—352).—A theoretical aper in which Planck's thermodynamical function is considered in onnexion with binary liquid mixtures with the object of obtaining xpressions which shall represent the equilibrium conditions of ich liquid pairs and give the saturation conditions. [See also ahn, A., 1902, ii, 597.] J. F. S.

Polymerism of Dissolved Binary Salts. P. WALDEN *Zeitsch. Elektrochem.*, 1920, **26**, 60—65).—The molecular weight f a number of binary salts has been determined by the cryoscopic

method at a series of concentrations in non-ionising solvents. As solvents, acetic acid, naphthalene, and diphenylamine were used, and as dissolved substances, tetra-amylammonium iodide, triphenylamylphosphonium iodide, tetrapropylammonium iodide, ammonium thiocyanate, tetramethylammonium thiocyanate, tetraethylammonium bromide, ethylammonium chloride, and tetraethylammonium iodide. From the results it is shown that depolymerisation occurs according to the expression $x = c^{1/3}$. const., that is, the degree of association is directly proportional to the linear concentration or to the distance between the molecules. The molecular weight, M, of the dissolved salt conditions the dimensions of the constant, since $x = 0{\cdot}305 M^{1/3}/V^{1/3}$ or $x = 0{\cdot}305 M^{1/3} . C^{1/3}$. The influence of the nature of the solvent is shown by the fact that the degree of association x *is inversely proportional to the dielectric constant* E of the solvent, as shown by the expression $x = 1{\cdot}92 \sqrt{M}/EV^{1/3}$ or $x = 1{\cdot}92 . M^{1/2}C^{1/3}/E$. In view of the influence of the dielectric constant in the depolymerisation, the author puts forward the question: Are the products of depolymerisation oppositely electrically charged according to the scheme:

$$(MX)_2 \rightleftharpoons (MX)^{\cdot} + (MX)' \rightleftharpoons (M_2X)^{\cdot} + X' \rightleftharpoons 2M^{\cdot} + 2X'?$$

J. F. S.

Influence of the Molecular Size of Electrolytes on the Conductivity and the Ionic Velocity of the Ions: Solvation of Ions in Non-aqueous Solutions. P. WALDEN (*Zeitsch. Elektrochem.*, 1920, **26**, 65—71).—It is shown that a large number of binary salts, mainly iodides, in a number of non-aqueous solvents follow the relationship $\lambda_\infty \eta_\infty \sqrt{M} = \text{const.} = 11{\cdot}15$, where λ_∞ is the limiting conductivity of a salt with molecular weight M in the solvent under investigation, and η_∞ is the viscosity of the solvent. If these salts are regarded as normal, that is, neither associated nor solvated, it becomes possible to determine the degree of solvation of other salts with a fair degree of accuracy. As a control of the values obtained from the formula deduced by Herzog from Einstein's relationship (A., 1911, ii, 23), $\lambda_\infty \eta_\infty V^{1/3} = \text{const.}$ may be used. Both equations give solvation values which are practically identical for the ions examined. J. F. S.

Is the Migration Velocity of the Ions of an Electrolyte Extremely Large when the Solvent is Capable of Forming Similar Ions? P. WALDEN (*Zeitsch. Elektrochem.*, 1920, **26**, 72—76).—A theoretical paper in which the conductivity and mobility of the ions of salts, which furnish one ion similar to one of the ions of the solvent, have been considered. The solvents considered are pyridine, formic acid, acetic acid, aniline, *m*-chloroaniline, nitromethane, methyl thiocyanate, hydrocyanic acid, ammonia, formamide, and nitric acid. The results show that the titular question is to be answered in the negative, and that if there is any influence of the solvent on the dissolved substance in this respect, it only occurs in a few exceptional cases. J. F. S.

Dissociating Powers of Free and Combined Water. G. FRED ORDEMAN (*Carnegie Inst. Pub.*, 1918, **260**, 119—127).—The conductivities of two isohydric solutions were measured, and the measurements repeated after the addition of a third salt (in three different concentrations). The following series of salts were used: (*a*) isohydric solutions of *M*-potassium chloride and 0·695*M*-calcium chloride, before and after the addition of sodium, potassium, ammonium, magnesium, calcium, or strontium chloride; (*b*) isohydric solutions of *M*-sodium chloride and 0·597*M*-calcium chloride, the addendum being sodium, ammonium, magnesium, calcium or strontium chloride, or potassium nitrate; (*c*) isohydric solutions of *M*-sodium nitrate and 0·681*M*-calcium nitrate, the addendum being sodium, potassium, ammonium, magnesium or calcium nitrate, or potassium chloride; (*d*) isohydric solutions of 0·5*M*-sodium nitrate and 0·310*M*-calcium nitrate, the addendum being as in (*c*); (*e*) isohydric solutions of *M*-potassium nitrate and 0·698*M*-calcium nitrate, the addendum being sodium, potassium or strontium nitrate, or potassium or sodium chloride. For every pair of solutions, the suppression of the conductivity is more pronounced in the hydrated solutions, showing that the added salt dissociates more in the non-hydrated solutions than in the comparable, isohydric solutions of the hydrated salts. The repression of the ionisation of the hydrated salts added is much greater than that of comparable quantities of non-hydrated salts in both isohydric solutions of every pair studied. A few added salts, having no common ion, show irregular results. The combined water (of hydration) in the solution of a hydrated salt is assumed to possess less ionising power than the uncombined water, hence the salt added would be less dissociated. The hydrated salts used as addenda are less dissociated than the other addenda, because the water of hydration now exists in both of any pair of solutions. The dissociation, however, is always less in the solution of the hydrated salt of any pair, because of the smaller dissociating power of the water of hydration already present in that solution.

CHEMICAL ABSTRACTS.

The Ultimate Structure of Isomorphous Substances. F. RINNE (*Centr. Min.*, 1919, 161—172).—From the results of the *X*-ray analysis of the crystal structure of a number of substances, the author has calculated the absolute atomic or molecular volumes of the substances comprising a number of isomorphous series. The substances dealt with are the cubic elements aluminium, copper, silver, gold, and lead, the rhombohedral carbonates of magnesium, calcium, manganese, iron, zinc, and cadmium, and the haloids of lithium, sodium, potassium, rubidium, and cæsium. From a comparison of the Röntgen-ray diagrams of a large number of minerals, which are usually isomorphous mixtures, with those of pure substances, it is concluded that there is no essential difference between their structures; that is, the *X*-ray evidence favours the view that in isomorphous mixtures the dispersity is so great that

it is highly probable that the vicarious constituents replace one another atom for atom or group for group in the lattice structure of the crystal. The importance for isomorphism of the chemical nature, and especially of the valency, of the vicarious atoms or atomic groups is insisted on. This factor is often of more importance in determining isomorphism or miscibility than molecular volume. Thus, in the case of the above elements, although the edge of the fundamental lattice is practically of equal length for aluminium, silver, and gold, and considerably less for copper, silver and gold are perfectly miscible together, but only slightly so with aluminium. In the case of the haloids of the alkali metals, the miscibility varies with the temperature to a much greater extent than would be expected were the dimensions of the fundamental lattices the ruling factor. The author regards the mixed crystal state as one intermediate between a physical mixture and a true chemical compound. E. H. R.

Von Weimarn's Theory of the Colloidal State. E. H. BUCHNER and J. KALFF (*Rec. trav. chim.*, 1920, **39**, 135—144).—The authors consider that von Weimarn's theory of corresponding states in the formation of precipitates is untenable. They show that his law giving the relationship between "the coefficient of precipitation," on which the form of the precipitate depends, the solubility of the substance precipitated, and the amount of the precipitate formed is incorrect in the cases of such precipitates as calcium fluoride, barium fluoride, and calcium sulphate in comparison with barium sulphate, and in the cases of silver chloride, bromide and iodide, and lead iodide. Further, that in the case of such precipitates as aluminium hydroxide, the conditions cannot be expressed by any formula. Whilst his theory may have some value qualitatively, his law of corresponding states is not confirmed by quantitative experiments. W. G.

Swelling and Solution of Aleuron. MARIAN O. HOOKER and MARTIN H. FISCHER (*Kolloid Zeitsch.*, 1920, **26**, 49—58).—The amount of swelling of aleuron (a mixture of plant proteins) occasioned by water, dilute solutions of hydrochloric, nitric, sulphuric, lactic, formic, and tartaric acids, hydrochloric acid mixed with various quantities of the chlorides of sodium, potassium, iron, aluminium, ammonium, copper, magnesium, calcium, and strontium respectively; hydrochloric acid mixed with potassium bromide, nitrate, iodide, acetate, thiocyanate, tartrate, and citrate respectively; and hydrochloric acid mixed with carbamide, methyl alcohol, ethyl alcohol, dextrose, and sucrose respectively, has been measured. The amount of aleuron dissolved by the above-named solutions has also been determined. A similar series of experiments has been carried out with sodium hydroxide solutions and with sodium hydroxide solution to which the above-named substances have been added. It is shown that aleuron behaves, as

regards its swelling and solution, in much the same way as gelatin, fibrin, blood serum, and gluten. It swells more in acid and alkali solutions than in water, but the amount of swelling does not run parallel with hydrogen- or hydroxyl-ion concentration. The swelling is reduced, not only by neutralisation of the acid or alkali, but also by the addition of neutral salts. The greater the concentration of the added salt, the greater the reduction of the swelling. Non-electrolytes do not influence the swelling in either acid or alkali solution. The solubility of aleuron in acids and in alkalis is also greater than in water, but it does not run parallel with the swelling. Some salts increase the solubility, whilst others reduce it in both acid and alkaline solutions, but there is no parallelism between solubility and swelling. The results indicate that hydration and solution of an albuminous substance or mixture of albuminous substances, although often connected and often occurring in the same sense, yet are not identical processes. Each follows its own particular laws. J. F. S.

Influence of the Concentration of Electrolytes on some Physical Properties of Colloids and Crystalloids. JACQUES LOEB (*J. Gen. Physiol.*, 1920, **2**, 273—296).—When alkali or neutral salt is added to a 1% solution of sodium gelatinate separated from distilled water by a collodion membrane, the rate of diffusion is diminished. This depressant action is greater when the cation of the added electrolyte is bivalent than when it is univalent. When a neutral $M/256$-solution of a salt with univalent cation is separated from distilled water by a collodion membrane, and an alkali or neutral salt is added, the diffusion of water is also depressed in proportion to the amount added. It can be shown that under these conditions water diffuses through the membrane in the form of positively charged particles. In the case of the diffusion of water into a neutral salt with univalent or bivalent cation, the effect of the addition of electrolyte on the rate of diffusion can be explained on the basis of the influence of the ions on the electrification and the rate of diffusion of the electrified particles of water. Since the influence of the addition of electrolyte seems to be the same in the case of solutions of metal gelatinate, the question arises whether this influence cannot also be explained in the same way, and, if this be true, the further question can be raised whether this depressing effect necessarily depends on the colloidal character of the gelatin solution, or whether in both cases the same property of matter is not being dealt with, namely, the influence of ions on the electrification and rate of diffusion of water through a membrane.

The curve representing the influence of the concentration of the electrolyte on the initial rate of diffusion of water from solvent into the solution through the membrane is similar to the curve representing the permanent osmotic pressure of the gelatin solution. The diffusion of water as negatively charged particles into a solution of gelatin chloride is depressed by addition of an acid or

neutral salt. This is also found to be true when the diffusion takes place into a solution of $M/512$-Al_2Cl_6. J. C. D.

Influence of a Slight Modification of the Collodion Membrane on the Sign of the Electrification of Water. JACQUES LOEB (*J. Gen. Physiol.*, 1920, **2**, 255—271).—Collodion membranes which have received one treatment with 1% gelatin solution show for a long time afterwards a different osmotic behaviour from untreated membranes. This difference shows itself only towards solutions of those electrolytes which have a tendency to induce a negative electrification of the water particles diffusing through the membrane. When solutions of salts with tervalent cation are separated from water by collodion membranes treated with gelatin, water diffuses rapidly into the solution, whilst no water diffuses when the collodion membrane has received no gelatin treatment. Solutions of acid separated from water by treated membranes show negative osmosis, whereas with untreated membranes positive osmosis occurs. These differences only occur in that range of concentrations of electrolytes inside of which the forces determining the rate of diffusion of water through the membrane are predominantly electrical, that is, from 0 to about $M/16$. The differences in the osmotic behaviour of the two types of membrane are not due to differences in permeability, but are rather due to the fact that water diffuses into solutions of tervalent cations or acids through gelatin-treated membranes as negatively charged particles, whilst in the case of non-treated membranes the charge is positive. Treatment of the membranes with caseinogen, egg-albumin, blood-albumin, or edestin has the same effect, but treatment with peptone from egg-albumin, alanine, or starch has no such effect. J. C. D.

Colloidal Electrolytes. Soap Solutions and their Constitution. JAMES W. MCBAIN and C. S. SALMON (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 44—65; *J. Amer. Chem. Soc.*, 1920, **42**, 426—460).—Colloidal electrolytes are solutions of salts in which an ion has been replaced by a heavily hydrated multivalent micelle carrying an equivalent sum total of electric charges, and also serving as an excellent conductor of electricity. This new class of electrolytes probably includes most organic compounds containing more than eight carbon atoms, and capable of forming ions, also acid and alkali solutions of proteins, dyes, indicators, sulphonates, soaps, alkali tungstates, zincates, tellurates, and silicates. The constitution of solutions of the sodium and potassium salts of behenic, stearic, palmitic, myristic, lauric, decoic, octoic, hexoic and acetic acids has been investigated. The vapour pressure and elevation of the boiling point have been ascertained by the dew-point method for solutions of the above-named salts at concentrations $0{\cdot}2N$—$3{\cdot}0N$. From the results, coupled with osmotic and conductivity data previously published (T., 1914, **105**, 435), the concentration of crystalloid constituents and the concentration of colloid constituents are deduced. It is shown that, in N-solutions,

in every case colloid material is present; in the case of the hexoate, 15% is present as colloid, whilst with potassium stearate, 99% is colloid. The amount of colloid decreases rapidly with decrease in concentration, and it apparently becomes inappreciable with $N/5$-laurate solutions. The ionic micelle are regarded as either (in the case of palmitate) an agglomeration of palmitate ions heavily weighted by water as a complex solvate, $(P')_n.(H_2O)_m$, or, and more probably, a collection of all, or nearly all, the colloid in the ionic micelle, $(NaP)_x.(P')_n(H_2O)_m$. J. F. S.

Penetration of Electrolytes into Gels. I. Penetration of Sodium Chloride into Gels of Agar-agar containing Silver Nitrate. WALTER STILES (*Biochem. J.*, 1920, **14**, 58—72).—The penetration of sodium chloride from solutions of various concentrations ($5N$—$0{\cdot}05N$) into agar gels has been followed by the indicator method. When silver nitrate is present in the gel, the entrance of sodium chloride into the gel is marked by the formation of silver chloride, and the progress of the chloride into the gel is indicated by the forward movement of the sharp line of demarcation between the silver chloride in the gel and the unprecipitated silver salt. The distance this line of demarcation has moved forward in any time is termed the penetration. It marks the position of a definite concentration of chloride, namely, the saturation concentration of silver chloride. The penetration of sodium chloride into agar gels containing silver nitrate is, within wider limits, proportional to the square root of the time. If P is the penetration in a time t, $P/\sqrt{t}=$ constant for any particular gel and any particular concentration of penetrating salt, and is termed the penetration factor. The rate of penetration is dependent on the initial concentration of the penetrating salt, the higher the concentration of the salt the more rapid the penetration. The concentration of the gel itself appears to exercise little influence on the rate of penetration, but, owing to the probability of actions between the silver salt and the gel, and hence doubt as to the true active concentration of the silver salt in the gel, the influence of concentration of the gel must be left an open question. In any case, the influence cannot be great in gels containing between 1 and 4% agar. The expression obtained by von Fürth and Bubanovič (A., 1919, ii, 13) to indicate the relationship between the penetration, time, and concentration of the penetrating salt only holds in very special cases and between narrow limits, and is even then only very approximate. The following more general empirical relationship is deduced, $P/\sqrt{t}=k\log c+k'$, where c is the initial concentration of the penetrating salt, k a constant depending on the nature of the penetrating salt and also, although to a slight extent, on the nature of the gel content, and k' a second constant depending mainly on the concentration of silver nitrate in the gel. J. F. S.

Adsorptive Stratification in Gels. III. SAMUEL CLEMENT BRADFORD (*Biochem. J.*, 1920, **14**, 29—41. Compare A., 1919, ii, 139).—A discussion of the supersaturation and the adsorption

theory of the Liesegang phenomenon in gels. The author supports the adsorption theory by a number of experimental facts. The formation of bands usually ceases long before the bottom of a tube is reached. The hypotonic reagent is invariably so strong that this effect can only be due to the solute in the gel having been exhausted from the lower regions of the tube. This fact also controverts the deduction from the supersaturation theory, that the diffusion of the solute in the gel is negligible.

With certain colloidal precipitates, such as manganese sulphide, in agar, a tendency is observed to form large spherical aggregates which have much the same structure and density as the bands, except that they frequently show concentric banding. When one of these spherical aggregates begins to form in the zone where a band will shortly appear, the band does not extend to join the sphere, but a spherical cavity, 2—3 mm. wide, is left surrounding the concretion, from which the surface of the cavity is everywhere equidistant. This effect must be due to the solute having been exhausted from the neighbourhood of the aggregate. Its spherical form implies that nutrient material has accrued equally from all directions. J. F. S.

Mutual Action of Sols. WILDER D. BANCROFT (*J. Physical Chem.*, 1920, **24**, 21—29).—A theoretical paper in which it is shown that when positively charged gelatin is mixed with a negatively charged sol, or negatively charged gelatin with a positively charged sol, there may be precipitation over a range of relative concentrations. When two sols, peptised by water, are mixed, the mutual adsorption may decrease the adsorption of water to such an extent that precipitation takes place. There may be, and often is, mutual adsorption when two sols having the same electrical charge are mixed. The mutual adsorption of positively charged ferric oxide and positively charged gelatin in ammonia solution gives a different product from the mutual adsorption of positively charged ferric oxide and positively charged gelatin to which ammonia is subsequently added, inasmuch as in the first case precipitation is brought about, whilst in the second there is no precipitation. J. F. S.

[Physical Chemical Analysis of Metal Hydrosols.] An Explanation. RICHARD ZSIGMONDY (*Kolloid Zeitsch.*, 1920, **26**, 67—69).—Polemical; an answer to Pauli's criticism (this vol., ii, 168) of certain parts of a paper by Varga. J. F. S.

Rôle of Valency in the Coagulation of Suspensoids by Electrolytes. WOLFGANG OSTWALD (*Kolloid Zeitsch.*, 1920, **26**, 69—81. Compare this vol., ii, 168).—The various theories which have been put forward to explain the function of valency in the coagulation of suspensoids are summarised, and the precipitation values of a large number of electrolytes are collected from various sources and tabulated. From the absorption theory of Freundlich,

an expression is deduced which gives a quantitative relationship between valency and precipitating power. This has the form $1/c_1:1/c_2:1/c_3 \ldots = 1:2^n:3^n \ldots$, in which c_1, c_2, and c_3 are the precipitating values of uni-, bi-, and ter-valent electrolytes, and n is a constant. It is shown that none of the theories hitherto put forward satisfactorily accounts for the coagulation of electrolytes. It is shown that the rôle of valency as the determining factor in coagulation processes has been considerably overestimated. This follows from the facts that (1) the precipitating values of electrolytes of the same valency differ considerably, (2) univalent electrolytes in some cases have smaller precipitating values than bivalent electrolytes, and (3) salts of different valencies fall into the same group with respect to their precipitating values. J. F. S.

Precipitation of Congo-rubin by Electrolytes. WOLFGANG OSTWALD (*Koll. chem. Beihefte*, 1920, **26**, 92—102. Compare A., 1919, ii, 187, 400).—A continuation of previous work (*loc. cit.*). It is shown that the behaviour of Congo-rubin toward electrolytes in respect of Schulze's rule is exactly the same as that of inorganic hydrosols. The behaviour of Congo-rubin in respect of its colour changes in the presence of electrolytes is of the same nature and depends on the same causes as the colour changes of inorganic hydrosols, for example, the colour changes of gold sols, or, in other words, the phenomenon is of colloidal chemical character.

J. F. S.

Equilibria in Solutions containing Mixtures of Salts. The System Water and the Chlorides and Sulphates of Sodium and Magnesium at 25°. W. C. BLASDALE (*J. Ind. Eng. Chem.*, 1920, **12**, [ii], 164—167).—Previous work on this subject indicates that the solid phases to be expected at 25° are $MgSO_4,7H_2O$, $MgSO_4,6H_2O$, $MgSO_4,H_2O$, $Na_2SO_4,10H_2O$, Na_2SO_4, $MgCl_2,6H_2O$, NaCl, and $MgSO_4,Na_2SO_4,4H_2O$ (blödite). In ascertaining the limits of the fields representing the composition of all the solutions which can be in equilibria with each of the eight solid phases, the composition of solutions saturated with respect to $MgSO_4,7H_2O$, $Na_2SO_4,10H_2O$, $MgCl_2,6H_2O$, and NaCl was determined, and the ends of two axes at right angles, one to represent the relative proportions of $MgSO_4$ and NaCl, and the other of Na_2SO_4 and $MgCl_2$, were fixed. The solubility of each of the former four salts in solutions containing increasing concentrations of a second salt which yields a common ion was determined up to the point at which a second solid phase appeared, and thereby a number of points intermediate between the extremities of the two axes, representing solutions in equilibrium with two solid phases, were fixed. Further, starting with solutions saturated with respect to two solids, the composition of solutions saturated with respect to each pair of solids, in the presence of increasing concentrations of that salt which yielded a fourth ion, was determined up

to the point at which a third solid separated. The results are shown in a curve, in which the horizontal axis is used to represent the number of mols. of $MgSO_4$ and NaCl, and the vertical axis the number of mols. of $MgCl_2$ and Na_2SO_4, per 1000 mols. of water, and tables are given showing the composition of all these solutions which represent critical points. S. S. A.

Reaction Isochore and Velocity of Reaction from the Statistical Point of View. M. POLÁNYI (*Zeitsch. Elektrochem.*, 1920, **26**, 49—54).—A theoretical paper in which it is shown that the velocity constant of a reaction of the type $A + B_2 \rightleftharpoons AB + B$ in the endothermic direction is given by the product of the number of collisions and the equilibrium constant, and in the reverse direction it is the same as the number of collisions. These results are deduced from the assumption that it is just as likely after a collision between A and B_2, that the particles react, or that they are dispersed without a reaction taking place. The results of the theoretical investigation are tested by means of the experimental results of Bodenstein and Lind on the reaction $Br + H_2 \longrightarrow BrH + H$ (A., 1907, ii, 76), and found to be in accordance with the experimental facts. J. F. S.

Influence of Pressure on the Temperature of Explosion. G. TAMMANN (*Nach. Ges. Wiss. Göttingen*, 1919, 220—224; from *Chem. Zentr.*, 1920, i, 146).—The explosive material is contained in a small glass tube open at one end, and is placed in a steel cylinder filled with mercury; the latter is connected with a spring manometer and pressure pump. The cylinder is heated in an oil-bath provided with an efficient stirrer, the temperature of the bath being observed from minute to minute. Tables are given showing the rate of heating in degrees per ten minutes before attaining the temperature of explosion, the weight of explosive, the pressure and temperature at which explosion occurs, the differences in pressure before and after the explosion, and the sudden rise of pressure during the explosion. The temperature of explosion of moist glyceryl nitrate varied somewhat considerably at constant pressure; increase of the latter by 2500 kilos. per sq. cm. appeared to depress the temperature of explosion by 8·4°, but the variation lies within the limits of experimental error. With dry glyceryl nitrate, the variations are less marked, but a distinct influence of the pressure on the temperature of explosion is not observed; a similar effect is still less certain in the case of a mixture of tetranitromethane (2 mols.) and benzene (1 mol.). With tetranitromethane (2 mols.) and naphthalene (1 mol.), an increase in pressure of about 2000 kilos per sq. cm. causes an elevation of 5·7° in the temperature of explosion. The influence of pressure on the temperature of explosion of liquid explosives is determined by the effect of pressure on the conductivity for heat of the material itself and its environment, and by alteration in the chemical-kinetic conditions, such as the increase in the number of molecular collisions caused by

isothermal increase in pressure as a consequence of the increase in volume of the explosive. H. W.

Difference in Chemical Activity of Free and Semi-combined Water as Illustrated by the Effect of Neutral Salts on the Hydrolysis of Acetic Anhydride. GERALD C. CONNOLLY (*Carnegie Inst. Pub.*, 1918, **260**, 131—143).—In extension of the work of Holmes and Jones (*ibid.*, 1915, **230**) on the effect of salts on the hydrolysis of methyl acetate and methyl formate, the action of strongly hydrated and of slightly hydrated salts on the hydrolysis of acetic anhydride has been studied with the object of determining whether any chemical difference exists between free and combined water. Care being taken always to keep the water content constant, *M*-, 0·5*M*-, and 0·25*M*-solutions of various salts (potassium, sodium, calcium, magnesium, barium, and strontium chlorides, sodium and magnesium sulphates, potassium and sodium nitrates) at 15° and at 25° were treated with acetic anhydride, aliquot portions were removed at various intervals, and the acetic acid estimated. The amount of acetic acid present in mixtures of the acid and its anhydride was estimated by adding aniline and titrating the total acetic acid with sodium hydroxide. The concentration of the anhydride was 5%, and in no case did the time exceed sixty minutes at 15° and forty minutes at 25°, since the hydrolysis by water was practically complete.

All the salts examined, excepting sodium and magnesium sulphates, have in the case of the greater concentrations a retarding influence on the hydrolysis, the retardation diminishing with increasing salt dilution. The four non-hydrated salts have practically the same retarding effect on the hydrolysis. The hydrated salts, excepting magnesium chloride, produce greater hydrolysis than the non-hydrated salts, and with the more dilute solutions there is an appreciable acceleration of the hydrolysis of the anhydride over that due to water alone. Sodium and magnesium sulphates at all concentrations have a marked accelerating effect on the hydrolysis. Calcium, strontium, and barium chlorides also exert an accelerating influence in the more dilute solutions. The results with magnesium chloride and sulphate were inconclusive, the former resembling the non-hydrated salts in retarding the hydrolysis at all dilutions. CHEMICAL ABSTRACTS.

The Alkaline Hydrolysis of Tartaric Ester. ANTON SKRABAL and ERNA SINGER (*Monatsh.*, 1919, **40**, 363—375).—The rate of hydrolysis of methyl tartrate by a mixture of sodium carbonate and sodium hydrogen carbonate has been measured, after the procedure necessary for the attainment of satisfactory results had been worked out in the case of methyl acetate. Referred to $[OH]' = 1$ and at 25°, the constants for the first and second stages in the hydrolysis of methyl tartrate are $k_1 = 206$ and $k_2 = 14·7$ respectively, whilst for methyl acetate $k = 5·4$. J. K.

Catalysis of Hydrogen and Oxygen Mixtures at the Ordinary Temperature by Moistened Contact Substances. II. The Platinum Metals as Hydrogen Carriers. K. A. HOFMANN and LOTTE ZIPFEL (*Ber.*, 1920, **53**, [*B*], 298—314. Compare Hofmann and Ebert, A., 1917, ii, 25).—The results may be summarised in the following manner.

Mixtures of oxygen and hydrogen are catalysed at palladium, platinum, or iridium surfaces at very different rates, depending on the exact extent, at the moment, to which they are charged with gas. Pre-treatment with oxygen is thirty to fifty times as effective in the case of palladium, three times with platinum, and three to ten times with iridium as is pre-treatment with hydrogen. The greater activity caused by charging with oxygen is not brought about by the adsorbed or occluded gas serving as a source for the formation of water, since the amount of metal required for catalysis is insufficient to produce this effect, but depends on the production of a "fresh" hydrogen–metal combination, which, in the cases of palladium and platinum, is far more active than an "aged" preparation. The catalyst shows greater activity in proportion as this "fresh" condition is more rapidly and completely developed. In the case of iridium, another factor is involved, since the metal, in presence of gases containing excess of oxygen, can *function as an active oxygen electrode.*

The close parallelism between catalytic and electromotive activity indicates that both effects are to be ascribed to the same cause. This probably depends on the presence of free or metallically-dissolved hydrogen atoms, which cause the hydrogen potential and ultimately combine with the oxygen of the gas mixture to form water. *Under the experimental conditions* adopted, an active oxygen electrode is only formed with finely divided iridium when the oxygen concentration is high; platinum and palladium behave entirely as hydrogen electrodes.

The maximal velocity of formation of water is not invariably observed when the gases are used in the proportion of hydrogen (2 vols.) to oxygen (1 vol.), but, according to conditions, may occur at a greater or smaller oxygen concentration, according as the catalyst becomes more or less rapidly saturated with hydrogen. If the catalyst can also function as an oxygen electrode, as in the case of finely-divided iridium, a second maximum may occur with a higher oxygen content in the gas.

It may be generally stated that the surface does not show its greatest catalytic activity when hydrogen and oxygen are absorbed according to the measure of their combination at an electrically neutral electrode, but that the maximum possible hydrogen or oxygen potential must be "freshly" developed in order to react with the gaseous mixture at the maximum rate. H. W.

A Relation among the Atomic Weights of Chemical Elements. SUMINOSUKE ONO (*Proc. Phys. Math. Soc. Japan*, 1919, 1, 231—236).—The atomic weight (*A*) may be given by a

formula, $A = N'^{\eta}$, where $\eta = 1{\cdot}204$ and N' is roughly equal to Moseley's atomic number $+2$ or Rydberg's ordinals. For the more exact calculation of the atomic weight, N'^{η} may become a more complicated function, and N' may be identical with neither the atomic numbers nor the ordinals. CHEMICAL ABSTRACTS.

The Derivation of Molecular and Atomic Weights from Vapour Densities in Chemical Teaching. W. MANCHOT (*Chem. Zeit.*, 1920, **44**, 153—154).—An academic discussion on the most suitable formulæ for expressing the relation between molecular weights and gas densities with respect to water, air, and hydrogen in teaching chemistry. E. H. R.

The Law of the Harmonic Triangle in Chemical Reactions. EDUARD SCHMIZ (*Ber. Deut. pharm. Ges.*, 1920, **30**, 27—33). —The numerical relationships shown in a previous paper to hold between the atomic weights of a number of the elements (A., 1919, ii, 460) are now shown to hold also between the atomic and molecular weights of substances taking part in simple inorganic reactions. These relationships are those holding between the sides and hypotenuse of an isosceles right-angled triangle, the radius of the inscribed circle and that of the circle circumscribed about the squares erected on the sides of the triangle. It is claimed that, in simple cases, unless such a relationship holds between the molecular weights of substances, interaction between them cannot take place. E. H. R.

Structure of the Atomic Nucleus. E. GEHRCKE (*Ber. Deut. physikal. Ges.*, 1919, **21**, 779—784).—A theoretical paper in which the author formulates the constitution of the nucleus of the helium, lithium, glucinum, boron, nitrogen, and carbon atoms. The helium nucleus consists of two electrons and four hydrogen ions. In the case of lithium, the nucleus consists of four electrons situated at the corners of a regular tetrahedron, and seven hydrogen ions situated one at the centre of gravity of the tetrahedron, one at each corner of the tetrahedron, and two in an orbit close to the tetrahedron and at some distance from the outer electron ring. This nucleus is capable of accounting for the doublet series of the lithium spectrum. Glucinum possesses a nucleus consisting of five electrons situated one at the centre of gravity and one at each of the corners of a regular tetrahedron, and nine hydrogen ions situated one in the middle of each of the edges of the tetrahedron and the remaining three in an orbit surrounding the tetrahedron. This nucleus is capable of explaining triplet series of the glucinum spectrum. Boron has a nucleus composed of six electrons situated one in the middle of each of the edges of a regular tetrahedron, and eleven hydrogen ions situated one at the centre of gravity of the whole, one on the outside of each of the nuclear electrons, and one at each of the corners of the tetrahedron. The nucleus of carbon consists of six electrons situated as in the case of boron, one in

the middle of each of the edges of a regular tetrahedron, and twelve hydrogen ions, two of which are attached to each of the electrons. A nucleus so constructed accounts for the tetrahedral directions of the carbon valencies, since it will possess four electrostatic lines of force in these directions. Nitrogen is regarded as having a nucleus composed of seven electrons and fourteen hydrogen ions, which are grouped into three helium nuclei in an orbit surrounding one electron with two hydrogen ions attached to it. Constructing, further, after the manner of nitrogen, the nucleus oxygen is regarded as a ring of four helium nuclei, fluorine as four helium nuclei in a ring round an H_3^+ ion, and neon as a ring of four helium nuclei round a single helium nucleus. J. F. S.

Condition of Dissociation of the Gases of the Fixed Stars. JOHN EGGERT (*Physikal. Zeitsch.*, 1919, **20**, 570—574).—A theoretical paper in which, on the basis of the Nernst heat theorem, the relationship between the dimensions of the chemical constants deduced by Sackur, Tetrode, and Stern, and the Bohr atomic theory, the degree of dissociation of the atoms into nucleus and electrons, possible at temperatures between 10^6 and 10^{7o} and pressures of 10^7 atm., is investigated. The calculations show that, considering only one type of atomic model, the maximum dissociation would consist in the separation of the two outermost rings of electrons, that is, of sixteen electrons. From this, it follows that the mean atomic weight of the gases of the fixed stars is 3·3, a value which is very near that (2·8) deduced by Eddington in his theory of the structure of the fixed stars. J. F. S.

Atomic Nuclei and α-Radiation. HANS TH. WOLFF (*Ann. Physik*, 1919, [iv], **60**, 685—700).—A theoretical paper in which a theory of the structure of the atomic nucleus and the forces operative in the nucleus is put forward. The nucleus has a disk-like form and is made up of concentric rings. With the exception of the outermost ring, they consist of singly charged hydrogen atoms and doubly charged helium atoms, which are rotating round the middle point. Outside these charged atoms, in the outermost ring, rotate the electrons. The positive charges are assumed to exert an attraction on one another when they are at certain distances apart, and thereby effect the stability of the nucleus. At small distances, however, a repulsive force becomes operative. On this assumption, it is shown that one of the two potential formulæ,

$$P = L(1/R - A_2/R^2 + A_3/R^3)$$

and $P = L(1/R - A_3/R^3 + A_5/R^5)$, represents the reciprocal action of the positive charges in the atomic nucleus. Expressions are deduced for calculating the potential and field of force which a rotating charge will generate in a point in the same plane, but in a ring outside itself. The conditions of stability after movement are worked out for a point which attracts a rotating charge according to either of the above formulæ. Both potential formulæ are applied to the atomic nucleus of the radium atom, and the constants

determined so that they are in keeping with the expulsion of an α-radiation of the experimentally determined velocity.

J. F. S.

Analysis of an Electron-transference Hypothesis of Chemical Valency and Combination. JOHN MARSHALL (*Proc. Roy. Soc. Edin.*, 1919, **39**, [3], 209—233).—A mathematical investigation of refractive indices based on the Thomson model atom, in which account is taken of the effect of the positive electrification as well as of the electrons, and of the fields of electrical action between the atoms of a molecule. The results are in moderate agreement with experiment. J. R. P.

The Octet Theory of Valence and its Applications with Special Reference to Organic Nitrogen Compounds. IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1920, **42**, 274—292).—The octet theory of valence, which has been described in previous papers (Lewis, A., 1916, ii, 310; Langmuir, A., 1919, ii, 506), is here applied particularly to organic nitrogen compounds, although the general application of the theory to inorganic nitrogen compounds and to salts is discussed.

The number of available electrons in the outside shell of any atom is usually given by the ordinal number of the column of the periodic table in which the element is found. The number, which may be represented by E, corresponds with the maximum positive valence of the ordinary valence theory, and is one for sodium, four for carbon, five for nitrogen, six for oxygen, and seven for chlorine. It is readily proved that the octet theory is entirely in agreement with the ordinary valence theory whenever the ordinary formulæ are based on valences of unity for hydrogen and $8-E$ for each other element. Thus the ordinary formulæ agree with those of the octet theory whenever the following valences are adopted: hydrogen, one; carbon, four; nitrogen and phosphorus, three; oxygen and sulphur, two; chlorine, bromine, etc., one. On the other hand, all formulæ in which valencies different from these have been used require modification according to the octet theory. The application of the octet theory to the following compounds, among others, the formulæ of which require modification, is particularly discussed: sodium chloride, Na^+Cl^- (the co-valence of both atoms is zero); ammonium chloride, $(NH_4)^+Cl^-$ (the nitrogen is quadricovalent); triphenylmethyltetramethyl ammonium, $(NMe_4)^+[CPh_3]^-$ the nitrogen is quadricovalent, whilst the central carbon atom in the anion is tercovalent); diazophenol, $R<^{O}_{N:N}$; diazonium compounds, $(R-N\equiv N)^+OH^-$ or $R-N\equiv N\cdot OH$; triazo-compounds, $R-N=N\equiv N$; hydroxylamine, $H_2N\cdot OH$ or H_3N-O.

According to this theory, all salts are completely ionised even before they are brought into solution. This conclusion is, moreover, in agreement with the recent work of Milner, Ghosh and

others; *it explains why there are weak acids and weak bases*, but no weak salts.

The known cases of isomerism, including stereoisomerism, of nitrogen, phosphorus, and sulphur compounds are in full accord with the octet theory.

The *fact that organic cyanates, cyanides, and nitrites exist in two* isomeric forms whilst the corresponding inorganic salts exist in only one form is explained, since the nulcovalent atoms of the metals in the inorganic compounds are not attached to definite atoms of the acid radicles.

The available data on phosphonium, arsonium, sulphonium, and oxonium compounds are in full accord with the octet theory, which gives for these compounds constitutions closely resembling those previously assigned by Werner. H. W.

Accelerated Filtration through Filter-paper. G. Bruhns (*Chem. Zeit.*, 1920, **44**, 207).—A filter-paper, folded in the usual way, is placed in a funnel, and the loose end of the three-fold layer is turned back and pressed against the side of the funnel; this folding back is repeated several times, so that the greater part of the interior of the funnel is covered by only one thickness of paper. In the ordinary way of using a filter, one-half of the funnel is covered by a threefold layer of paper. W. P. S.

Small Generator for Acetylene Bunsen Burners. P. Askenasy (*Zeitsch. Elektrochem.*, 1920, **26**, 32).—An acetylene *generator is designed which with one charge of carbide will feed a* large bunsen burner with acetylene for six hours. J. F. S.

[Lecture Experiment.] A Chemical Model of the Excitation Process. Max Verworn (*Pflüger's Archiv*, 1917, **167**, 289—308).—A mixture of pure, vacuum-distilled nitric acid and 40% formaldehyde solution possesses considerable lability, and will react with explosive violence by the action of certain stimuli. The reaction is an oxidative decomposition of the formaldehyde to carbon dioxide and water. The mixture will remain unchanged at ordinary temperatures, but on addition of nitrous oxide, colloidal platinum, or on warming there is first a latent period during which no change occurs, which is followed by the violent reaction. Cooling the mixture, or the addition of water, or a carbamide solution will inhibit the process. If the mixture is placed in a long tube, *and one part is locally stimulated, the reaction will proceed along* the whole tube in the form of a wave. The mixture is an "isobolic" system, and obeys the "all or nothing" law. J. C. D.

Inorganic Chemistry.

Heat of Vaporisation of Hydrogen. W. H. KEESOM (*Zeitsch. Sauerstoff Stickstoff Ind.*, 1919, *ii*, 83; from *Chem. Zentr.*, 1920, i, 147).—Dewar has determined the heat of vaporisation of hydrogen to be 123*WE*; the author, however, gives the values 108·5—113·2, the greater probability of which is supported by theoretical considerations. H. W.

Crystallography of Ice. F. RINNE (*Ber. Verh. Sächs. Ges. Wiss., Math.-Nat. Kl.*, 1917, **69**, 57—62; from *Jahrb. Min.*, 1919, *Ref.* 25—27).—The *X*-ray photograph of ice on the basal plane shows dihexagonal symmetry with $a:c=1:1·678$, but does not decide whether the crystal is hemimorphic or not. Ice belongs to the magnesium type of the author's "isotypes" (A., 1916, *ii*, 29), of which a tabulated list is given. L. J. S.

Vapour Pressure of Solid Bromine. TEÓFILO ISNARDI (*Ann. Physik*, 1920, [iv], **61**, 264—272).—The vapour pressure of solid bromine has been determined at 0°, −10·9°, −15·5°, and −21·1° by two methods: (1) a manometric method, and (2) by allowing the vapour of bromine at measured temperature to fill a globe of known volume, condensing and weighing the liquid. The values obtained are considerably higher than those determined by Ramsay and Young (T., 1886, **49**, 453), except in the case of the value at 0°, which lies very near to that of Ramsay and Young. The following values are obtained: 0°, 65·83 mm.; −10·9°, 35·37 mm.; −15·5°, 24·95 mm.; and −21·1°, 15·75 mm. Extrapolation of the vapour-pressure curve to −41·3° gives values which agree very closely with those obtained by Cuthbertson by his optical method (A., 1911, ii, 582). The triple point is calculated to lie at −7·3° and 46·4 mm. pressure. The vapour pressure of solid bromine is given by the formula $\log p = a/T + b\log T + c$, where the constants have the values $a = -7109·142$, $b = -43·33195$, and $c = 133·46929$. The heat of sublimation is calculated to 60·7 cal. per gram. J. F. S.

Revision of the Atomic Weight of Fluorine. E. MOLES and T. BATUECAS (*J. Chim. Phys.*, 1919, **17**, 537—588).—See this vol., i, 283.

Mass of the Litre of Air and Gas Mixtures. A. LEDUC (*Engineering*, 1919, **108**, 569).—A résumé of the more important of the results published by Leduc (*Trav. Mem. Bureau Internat. Poids et Mesures*, **16**). Two gases, *A* and *B*, both at pressure *P* and of equal volume, when mixed in double the volume have not the same pressure as before mixing, but a pressure $P+\epsilon+\epsilon_1$, where ϵ and ϵ_1 depend on the nature of the gases. If the two gases are similar chemically, $(\epsilon+\epsilon_1)$ is immeasurable, as, for example, is the

case with a mixture of carbon dioxide and nitrous oxide, but in the case of hydrogen and sulphur dioxide the mixture has a pressure 3 mm. greater than the pressure of the constituents. As regards the mixture of oxygen and nitrogen in the atmosphere, ϵ may be disregarded. The density of air has been determined by direct weighing of air and from the weight of the constituent gases. Paris air has the following composition by volume (carbon dioxide and water vapour having been removed): oxygen, 0·2100; nitrogen, 0·7806; argou, 0·0094; neon, 15×10^{-6}; helium, 5×10^{-6}; hydrogen, 1×10^{-6}; krypton, 50×10^{-9}, and xenon, 6×10^{-9}; by weight: oxygen, 0·2321; nitrogen, 0·7549; argon, 0·0130; neon, $8{\cdot}4 \times 10^{-6}$; helium, $0{\cdot}7 \times 10^{-6}$; hydrogen, $0{\cdot}07 \times 10^{-6}$; krypton, 140×10^{-9}; and xenon, 30×10^{-9}. The rare gases, with the exception of argon, only affect the density of air in the fifth decimal place. A litre of air at 0° and 760 mm. weighs 1·2928 grams when $g = 980{\cdot}665$; under a pressure of 1 megabar, if g is 980·97 and the density of mercury is 13·5951, the weight is 1·2759 grams. Samples of air collected all over France and Algiers and at various altitudes show a weight percentage of oxygen varying between 23·05 and 23·25%. The oxygen percentage is lower in the north of France, and there is generally less oxygen close to the soil than at the height of foliage. J. F. S.

Equilibrium in the System Ammonia-Ammonium Thiocyanate. H. W. Foote and M. A. Hunter (*J. Amer. Chem. Soc.*, 1920, **42**, 69—78).—With the object of finding an absorbent other than water for free ammonia, the system ammonia–ammonium thiocyanate has been investigated. The vapour pressure of *ammonia–ammonium thiocyanate mixtures* has been determined by passing ammonia at known pressure through a known weight of ammonium thiocyanate until no further increase in weight occurred; in this way the vapour pressure of ammonia is known. This was carried out at temperatures 0—40°. A further series of vapour-pressure measurements was made for saturated aqueous solutions of ammonia and ammonium thiocyanate at temperatures −78° to +20°, and the following values obtained: −78°, 1 mm.; −65°, 4 mm.; −50°, 9 mm.; −34°, 21 mm.; −23°, 34 mm.; −20°, 41 mm.; 0°, 107 mm.; and +20°, 225 mm. The solubility of ammonium thiocyanate in ammonia has been determined at temperatures from 0° to 50°, and the following composition of saturated solutions is obtained: 0°, 23·3% ammonia, 76·7% thiocyanate; 10°, 22·65% ammonia, 77·35% thiocyanate; 20°, 21·6% ammonia, 78·4% thiocyanate; 30°, 20·15% ammonia, 79·85% thiocyanate; 40°, 18·4% ammonia, 81·6% thiocyanate; 50°, 16·65% ammonia, 83·35% thiocyanate. The specific conductivity of several solutions at 0° has been measured and the following values obtained: 75 mol. % ammonia, 0·1979 $ohms^{-1}$; 68·9 mol. % ammonia, 0·1640 $ohms^{-1}$; 63·3 mol. % ammonia, 0·1395 $ohms^{-1}$; 59·7 mol. % ammonia, 0·1246 $ohms^{-1}$; and 57·1 mol. % ammonia, 0·1110 $ohms^{-1}$. The vapour pressures found are much lower than Raoult's law requires. The practical application of ammonium thiocyanate as an absorbent

for ammonia has been considered, and it is shown that such an absorbent could be used in cases where it is necessary to eliminate water, and that a very large amount of the ammonia (98·1—99·6%) would be easily recoverable. J. F. S.

Catalytic Oxidation of Ammonia to Nitric Acid. B. NEUMANN and H. ROSE (*Zeitsch. angew. Chem.*, 1920, **33**, 41—44, 45—48, 51—55).—The authors have summarised the numerous processes and research in connexion with the catalytic oxidation of ammonia, and contribute some further results of investigations. Highest yields are obtained with platinum at 500° (96%), ferric oxide at 670° (90%), and iron–bismuth oxide at 600° (95%). The influence of the ammonia concentration, of the velocity of the gases, and of the temperature is discussed. Curves are given for the gas composition with various catalysts between 300° and 700°. Under definite conditions the oxidation will proceed continuously without external heat. W. J. W.

Vapour Pressure of Arsenious Oxide in Sulphuric Acid Solutions. F. SCHWERS (*J. Soc. Chem. Ind.*, 1920, **39**, 33—34T).—In the contact process for the manufacture of sulphuric acid, the sulphur dioxide is washed by bubbling through sulphuric acid. Experiments were made to determine to what extent arsenious acid is removed from the sulphuric acid by the sulphur dioxide, since any appreciable amount so carried forward would have a serious poisoning effect on the catalyst. In the experiments a measured volume of air was bubbled through sulphuric acid at 60° containing a known amount of arsenious oxide, and was then passed through a series of sodium hydroxide absorption tubes to collect any volatilised arsenic. The acid used contained, in two experiments, 0·015% and 0·001% of arsenious acid, and in each case small but appreciable amounts of arsenic were found in the absorption tubes, the amount carried forward being proportional to the amount present in the acid, and more than sufficient to have a poisoning effect on the catalyst. E. H. R.

Atomic Weights of Boron and Fluorine. EDGAR F. SMITH and WALTER K. VAN HAAGEN (*Carnegie Inst. Pub.*, 1918, **267**, —63).—Methyl alcohol obtained by the hydrolysis of methyl oxalate was used to prepare methyl borate, from which boric acid was produced by hydrolysis. The acid thus obtained and sodium carbonate gave borax, which was completely dehydrated by prolonged fusion. The anhydrous borax, by treatment with the appropriate acid and repeated evaporation with methyl alcohol, was converted into sodium chloride, sulphate, nitrate, and carbonate, from the weights of which the atomic weight of boron was calculated. The anhydrous borax was also indirectly converted into sodium fluoride through the formate, the direct conversion being impracticable.

The values obtained are 10·900 for boron and 19·005 for fluorine.

The boron value is 1% lower than the accepted value, which is erroneous owing chiefly to the retention of water by borax glass.
CHEMICAL ABSTRACTS.

The Combustion of Wood Charcoal with Nitric Acid. FRIEDRICH C. G. MÜLLER (*Zeitsch. angew. Chem.*, 1920, **33**, 40).—Wood charcoal was heated in a current of nitric acid vapour and the resulting gases were collected and analysed. The gases had approximately the following composition: CO_2, 57·2%; CO, 13·3%; H_2, 4·6%; N_2, 24·9%. The high carbon monoxide content and the presence of free hydrogen are noteworthy. It was observed that a considerable quantity of ammonia was present in the condensate. The production of ammonia is difficult to account for, as the reaction temperature was at least 1000°. E. H. R.

Adiabatic Compression of Carbon Dioxide at High Temperatures. KURT NEUMANN (*Zeitsch. Ver. deut. Ing.*, 63, 1002—1007; from *Chem. Zentr.*, 1919, iii, 989).—The author has investigated the expansion of carbon dioxide which, enclosed in an insulated cylinder, had previously been heated to such a temperature that partial dissociation into carbon monoxide and oxygen had occurred (a phenomenon which is observed in internal combustion engines). During the expansion, combination of carbon monoxide and oxygen to carbon dioxide (after combustion) takes place, which has an important influence on the adiabatics. Expressions have been developed which permit the calculation of gaseous composition, pressure, and volume at a definite temperature. H. W.

Aqueous Solutions of Carbon Dioxide. ROBERT STROHECKER (*Inaug.-Diss. Marburg*, 44 pp.; from *Jahrb. Min.*, 1919, *Ref.* 1).—Carbon dioxide solutions are important agents in geological processes. The slow neutralisation of such solutions by various bases was investigated, with the idea of gaining some idea as to their constitution. It appears that carbonic acid is not such a weak acid as is generally supposed, the dissociation constant being much higher than is usually stated. The acid constant was determined as $k=44\cdot10^{-5}$; it behaves, therefore, as an hydroxyformic acid.
L. J. S.

Fall in Pressure, Density, and Heat of Vaporisation of Argon. C. A. CROMMELIN (*Zeitsch. Sauerstoff Stickstoff Ind.*, 1919, **11**, 81—83; from *Chem. Zentr.*, 1920, i, 147).—The latent heat of vaporisation of argon at $-185\cdot5°$ is found to be 69·4*WE*. Values for the fall in pressure and density at numerous temperatures are given in tabular form. H. W.

Surface Colours of Metals. G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1919, 225—236; from *Chem. Zentr.*, 1920, i, 148).—Metals which yield surface colours become coated with a film of oxide, the rate of thickening of which with the time can be estimated by the alteration of the surface colours. Certain metals yield similar colours with iodine vapour at the ordinary tempera-

ture, and these are particularly suitable for the experimental investigation of the laws governing the rate of formation of the surface layer. The isothermal rate depends solely on the coefficient of diffusion of iodine into the layer of silver iodide covering the silver, and hence there is a parabolic dependence of thickness on time of action. The author's theory, which is confirmed by experiment, is based on the same fundamental ideas as Nernst's theory of solution. The actual chemical action occurs far more rapidly than the diffusion process, which, in the one case, leads to an attack of the reagent on the metal through a layer of constantly increasing thickness, whilst, in the other case, action occurs through a layer of constant thickness, since the deposit becomes detached. The quantitative relationships therefore depend on the different properties of the layers of reaction products. If crystals of iodine are placed in a desiccator over sulphuric acid, iodine vapour is observed which give surface colours with silver, copper, lead, and thallium; bismuth and antimony rapidly darken, and a fine, dark dust is deposited on their surfaces. Tin behaves similarly, but yields a yellow, incoherent layer. Small patches are formed within a few minutes on iron, cobalt, nickel, and manganese, and these, when removed from the desiccator, rapidly form droplets since the iodides are hygroscopic. Zinc and cadmium are more regularly, but much more slowly, attacked; with chromium, action is doubtful. With metals which give surface colours, the rate of increase of the layer which causes the coloration can be determined if care is taken to keep the concentration of iodine vapour constant. For this purpose air is drawn through a definite iodine solution, and the surface colour is compared at definite intervals with a table which gives the relationship between surface colour and thickness of film. A strip of silver shows three different types of behaviour towards iodine according to whether it has been rolled and cleaned, has been melted and thus covered with large crystallites, or has been left unworked and thus covered with multitudinous, small, dendritic crystals. The surface colorations on copper are similar to those on silver which has been similarly treated. Since, however, the index of refraction of copper iodide has not been determined, the thickness corresponding with the colours of the corresponding layers of air cannot be calculated to actnal thicknesses of iodide film. In many regions of temperature, the rate of increase of the superficial layer is independent of the temperature; this is true in the case of steel, for which the author gives calculations based on Löwenherz's experiments. H. W.

Segregation Dispersoids in Anisotropic Media. WILHELM EITEL (*Centr. Min.*, 1919, 173—183).—When homogeneous mixtures of sodium and potassium chlorides are cooled rapidly from a high temperature, metastable, homogeneous mixed crystals can be obtained which, however, when maintained for some time at a suitable temperature, decompose into the constituent salts, the crystals becoming opaque. This phenomenon has been investigated by the

ultramicroscopic method used by Lorenz and Eitel for the examination of metallic fogs in crystals of the corresponding chlorides (A., 1915, ii, 260, 261). A complete series of mixtures of the two salts was examined, and it was shown that the segregation of the mixture can be optically demonstrated under the ultramicroscope through the gradual formation of a fog or fine dispersoid phase at a temperature of about 250°. A number of photographs are reproduced. E. H. R.

Solidification Points of Mixtures of Metallic Chlorides. FRED. C. A. H. LANTSBERRY and R. A. PAGE (*J. Soc. Chem. Ind.*, 1920, **39**, 37—41T).—The authors have determined the freezing-point curves of the three binary mixtures and one ternary mixture comprised in the system sodium chloride–potassium chloride–calcium chloride by the cooling method, that is, plotting the cooling curve of a mixture of known composition and noting the arrest point. In the sodium chloride–potassium chloride series the components form a continuous series of solid solutions; the lowest melting mixture contains 55% KCl and 45% NaCl, and solidifies at 650°. The curve for the sodium chloride–calcium chloride series shows a very sharp minimum at 72·5% $CaCl_2$ and 27·5% NaCl; the corresponding freezing point is 505°. The potassium chloride–calcium chloride series is more complicated. The curve shows two distinct eutectic points and a maximum between them at about 70% $CaCl_2$. The maximum corresponds with a freezing point of 725° and represents the formation of a compound, $2KCl,3CaCl_2$. The eutectic between the compound and $CaCl_2$ freezes at 608° and contains 17·5% KCl, whilst that between the compound and KCl freezes at 590° and contains 60% KCl. The results do not confirm the work of Menge (A., 1911, ii, 982), who reported the formation of a compound, $4NaCl,CaCl_2$, in the sodium chloride–calcium chloride series. Freezing-point determinations were made on a series of forty-one ternary mixtures, and the results are plotted on a triangular diagram in which the isothermal lines are shown. There are two ternary eutectics, one containing 70% $CaCl_2$, 25% NaCl, and 5% KCl, freezing at 495°, the lowest in the series, the other containing 30% $CaCl_2$, 20% NaCl, and 50% KCl, freezing at 530°. E. H. R.

Additive Products of Sulphur Dioxide and Alkali Iodides (Alkali-iodide Sulphones). FRITZ EPHRAIM (*Ber.*, 1920, **53**, [*B*], 118).—The alkali iodides absorb varying proportions of sulphur dioxide (A., 1916, ii, 614), whereas Forcrand and Taboury have recently stated that sulphones of the type $MI,3SO_2$ are produced (A., 1919, ii, 341). J. C. W.

The Dissociation of Ammonium Carbamate. C. MATIGNON and M. FRÉJACQUES (*Compt. rend.*, 1920, **170**, 462—464).—The values obtained by Naumann (this Journ., 1871, 1195) for the dis-

sociation pressures of ammonium carbamate over the temperature range $-15°$ to $+60°$ may be expressed by two equations:

$$\log p = -3{\cdot}635/T - 7{\cdot}045 \log T + 28{\cdot}692$$

and

$$\log p = -4{\cdot}821/T - 15{\cdot}4 \log T + 53{\cdot}3586.$$

Measurements made at 81° and 93°, where the pressures are several atmospheres, confirm the accuracy of these equations. Calculations made by means of these equations give the heat of dissociation of ammonium carbamate, at constant pressure, as $-39{\cdot}0$ cal., which is in close agreement with the value previously found by experiment (compare Matignon, A., 1908, ii, 465). W. G.

Growth Phenomena of Copper, Silver, and Gold. A. BEUTELL (*Centr. Min.*, 1919, 14—28).—When natural or artificial silver sulphide is heated in an evacuated sealed tube for several days at a temperature of 350—600° a certain amount of decomposition takes place. The small amount of silver formed seems to wander through the silver sulphide, appearing at the cooler end of the tube in the form of hair silver. A number of experiments which were made showed that neither silver foil nor hair silver is attacked by sulphur vapour in a vacuum at 450°; the metal remained bright after forty-eight hours. Silver foil heated alone in a vacuum for a long period at 450—585° showed no trace of the growth of hair silver, but when silver foil and silver sulphide were heated together at 450° remarkable growths were obtained in a comparatively short time. To obtain these growths it is necessary for the silver and the silver sulphide to be actually in contact. Similar growths of copper were obtained by heating together copper and cuprous sulphide, but the process was much slower. When silver selenide or telluride was used in place of the sulphide, similar growths of silver were obtained, and hair copper was obtained to a certain extent with copper selenide and telluride. With gold, the best results were obtained when gold telluride containing silver was heated with silver foil. After seven days' heating at 500°, growths of "moss" gold containing silver had appeared at the cooler end of the tube. E. H. R.

Action of Water on Strontium Sulphide. E. TERRES and K. BRÜCKNER (*Zeitsch. Elektrochem.*, 1920, **26**, 25—32).—The action of water on strontium sulphide has been investigated. It is shown that the reaction in this case differs materially from the reaction in the case of barium sulphide (see following abstract). In the present case the reaction takes place between two molecules of water and two molecules of sulphide with the formation of equimolecular quantities of strontium hydroxide and strontium hydrosulphide: $2SrS + 2H_2O = Sr(SH)_2 + Sr(OH)_2$. The hydroxide and hydrosulphide, in consequence of their widely differing solubility, may be completely separated by crystallisation. When strontium sulphide is extracted with hot water and the clear filtrate cooled, pure strontium hydroxide crystallises. The solubility of strontium

hydrosulphide has been determined at temperatures 0—100°, and the following values obtained in grams of the anhydrous compound per 100 grams of water: 0°, 27·5; 20°, 29·7; 40°, 31·6; 60°, 33·2; 80°, 35·6; 100°, 37·8. The solubility of strontium hydroxide and strontium hydrosulphide in the same solution has been determined over the range 0—100°, and it is shown that no mixed compound is formed and that the hydroxide and hydrosulphide are in equilibrium with one another at all temperatures. Hence strontium hydroxide may be prepared by direct crystallisation of the solution obtained by the action of water on strontium sulphide. J. F. S.

Action of Water on Barium Sulphide. E. TERRES and K. BRÜCKNER (*Zeitsch. Elektrochem.*, 1920, **26**, 1—24).—The conditions influencing the formation of barium hydroxide from barium sulphide are experimentally investigated. A long list of patents and investigations is given with short critical remarks. A number of processes are repeated which are based on the action of water on barium sulphide and in which the crystalline product is worked up to barium hydroxide either by crystallisation or by treatment with metallic oxides. The results confirm in many cases the published accounts. The concentration of the solution and the composition of the residue obtained by extracting barium sulphide with water at various temperatures, are investigated. The content of the solution of barium hydroxide and barium hydrosulphide increases rapidly with increasing temperature. The solid residue consists to the extent of ⅓—½ of barium oxide. The solutions contain equal molecular quantities of hydroxide and hydrosulphide, so that it would appear as though in the presence of one another these substances had the same solubility in water. The action of barium hydroxide solution on barium sulphide shows, however, that the solution is not saturated with barium hydroxide. Hence it would seem that the solution is saturated with an intermediate compound, either an hydroxyhydrosulphide or a double compound of barium hydroxide and barium hydrosulphide, but it is not saturated with the components of this double compound. The solubility of barium hydrosulphide is determined from −15° to 100°. It is shown that the intermediate compound is formed when barium hydroxide and barium hydrosulphide are mixed in definite proportions, and that the maximum quantity of the compound is precipitated when twenty-seven molecules of the hydrosulphide are mixed with one molecule of the hydroxide; also the greater the excess of hydrosulphide the purer the precipitated double compound. The double compound may be expressed by one of the formulæ

$$OH{\cdot}Ba{\cdot}SH,5H_2O$$

or $Ba(OH)_2,Ba(SH)_2,10H_2O$. Experiments on the solubility of the intermediate compound show that the solution contains the components in very different proportions to the solid substance, that is, the undissolved residue contains an excess of hydroxide. The intermediate compound is shown to possess a considerable stability except towards oxidising agents, and there is no considerable decom-

position by water either with or without pressure or even by alkalis. The compound in relation to the hydrosulphide possesses a very small hydrogen sulphide pressure. For these and other reasons the author allots the formula $OH{\cdot}Ba{\cdot}SH,5H_2O$ to this compound. The solubility of barium hydroxide and barium hydrosulphide simultaneously has been determined from the cryohydric point to 100°. At all temperatures the region of existence of the double compound lies between those of barium hydroxide and barium hydrosulphide. The two simple compounds, therefore, can never exist together in the same solution, but must combine to form the intermediate product. It also follows that pure barium hydroxide can never be crystallised from the solution obtained by the action of water on barium sulphide. J. F. S.

Solubility of Zinc in Cyanide Solutions. H. A. White (*J. Chem. Met. Min. Soc. S. Africa*, 1919, **20**, 97—101).—From the results of an investigation made to determine the effect of various practical conditions on the solution of zinc during the precipitation of gold from cyanide solutions, it is concluded that close regulation of cyanide strength, alkalinity, and aeration of the auricyanide solution is necessary if the consumption of zinc is to be kept within reasonable limits. The ideal of a zinc consumption corresponding even approximately with the amount of gold precipitated appears unlikely to be attained. [For further details, see *J. Soc. Chem. Ind.*, 1920, April.] W. E. F. P.

Attempt to Determine if Common Lead could be Separated into Isotopes by Centrifuging in the Liquid State. J. Joly and J. H. J. Poole (*Phil. Mag.*, 1920, [vi], **39**, 372—375). —Molten lead has been centrifuged at a rate of 9000 revolutions per minute in electrically heated steel tubes for periods of one hour. The top and bottom layers were then withdrawn and cast into pellets, and the density determined. Although small differences between the density of the two layers are observed, they lie inside the experimental error, so that the experiments furnish no evidence that a separation of the isotopes has been effected.
J. F. S.

Effect of Centrifuging certain Alloys while in the Liquid State. J. Joly and J. H. J. Poole (*Phil. Mag.*, 1920, [vi], **39**, 376).—Using the method described above (see preceding abstract), it is found that silver–lead alloys could not be appreciably separated by centrifuging, but lead–tin alloys could be to some extent separated. Thus with an alloy containing 82% of lead and 18% of tin the top layer was 1·8% lighter than the bottom layer after centrifuging. J. F. S.

The Action of Water on Lead. J. F. Liversege and A. W. Knapp (*J. Soc. Chem. Ind.*, 1920, **39**, 27—33T).—The experiments here recorded on the action of water on lead were made with the waters collected in the Caban reservoir, Elan Valley, Wales, for

the use of Birmingham. These waters have a slight alkalinity, due to hydrogen carbonates, etc., equal to about 0·3 part $CaCO_3$ per 100,000. The action of such waters, and generally of waters the alkalinity of which does not exceed 1·5, is erosive. The whole surface of the lead is attacked and a flocculent precipitate forms. which, becoming detached, leaves the surface of the lead bright but mottled. When the alkalinity is increased to 1·5—2·5 the action becomes corrosive, and a loosely-held, white, opaque crust forms here and there on the surface. With still greater alkalinity the lead almost invariably becomes covered with a dull white film, which appears to act as a protective coating. The erosion tests were made by the method of Houston, in which a clean strip of lead of standard size is immersed in the water in a test-tube, air having free access. The amount of lead eroded is determined colorimetrically as sulphide. It proved possible to carry out the test in one day. It was found that such variations as occurred naturally in the amount of oxygen present in the water had no appreciable effect on the erosion. Variations in the amount of water used did not affect the amount of erosion, but the greater the depth of immersion of the lead the smaller was the velocity of attack. Exposure to glass lowered the erosive ability of the water. Erosion readily occurred in waters free from carbon dioxide, and small variations in the carbon dioxide content had no appreciable effect. The presence, however, of from 1 to 2% of carbon dioxide by volume caused a sudden change from erosion to "plumbo-solvency," that is, the lead precipitate no longer appears but soluble lead hydrogen carbonate is formed. Carbon dioxide dissolves lead more rapidly in presence of oxygen than alone. It is concluded that, given oxygen present, the principal factor in determining both amount and kind of erosion is the alkalinity of the water. The addition of small quantities of calcium hydroxide, carbonate, or hydrogen carbonate or of potassium permanganate decreases erosion, but calcium hydrogen carbonate is most effective; erosion occurs in absence of bacteria. It was observed that the bacteria in the water are not all destroyed by exposure to lead for six hours. E. H. R.

The Alloys of Copper, Zinc, and Nickel. Léon Guillet (*Compt. rend.*, 1920, **170**, 460—462).—Brasses containing nickel, in which the copper content falls to 40% and even less and the nickel content rises to 15%, are of particular interest because of their mechanical properties. Their breaking strain varies from 45 to 75 kilos./mm.^{2} with elongations of 45—18%. They are readily malleable at high temperatures, and in colour and resistance to oxidation they are comparable to German silver. W. G.

Compressibility of Indium. Theodore W. Richards and Jitsusaburo Sameshima (*J. Amer. Chem. Soc.*, 1920, **46**, 49—54). —The compressibility of indium has been determined over the pressure range 100—500 megabars. The measurements were made

ıt 25°. At this temperature indium has a density 7·318. The neasurements were carried out by the usual method, but instead ıf a steel piezometer, as previously used, a small glass one was nade use of in the present work. It is found that the compressiıility of indium over the range examined is 0·0000027, or about wo-thirds that of mercury. J. F. S.

The Limits of the Combining Power of Silicon with ertain Metals of the Iron Group. A. SANFOURCHE (*Rev. Mét.*, 1919, **16**, 239—245; from *Chem. Zentr.*, 1920, i, 149—150).—The uncertainties in the literature concerning the combining power ıf silicon with members of the iron group are frequently to be scribed to faulty methods of analysis consisting in the treatment ıf the alloy with alkaline reagents to effect removal of the excess ıf silicon and isolation of the alloy richest in silicon from the esidue. Actually, the persilicated compounds are frequently ttacked in the circumstances, whilst removal of the free silicon nclosed in the alloy is frequently incomplete. In addition, the ombining power of silicon with iron and related substances is ot a constant quantity, but depends on various factors, notably n the excess of free silicon. In ferrosilicons, the lower limit of ombining power lies at 55·55% Si, corresponding with the formula Fe_2Si_5, the upper limit at 60% Si corresponding with $FeSi_3$. With ıanganese–silicon alloys the limit lies between 46·70 and 50·11% Si; he upper value is here obtained with 8% of free silicon, whilst for ron, in similar circumstances, a 2% excess of silicon suffices. The igher limit approximates to the formula $MnSi_2$, so that this compound may be regarded as having the highest possible silicon conınt; the lower limit does not correspond with a definite compound, hilst the substance $MnSi_2$ appears to require the presence of a ıfficient excess of silicon to prevent its dissociation with liberation f this element. The influence of silicon is also very noticeable ith cobalt silicon alloys; as it increases from 0% to 6% the comining power increases from 50% to about 53%. Neither limit orresponds with a definite chemical compound; the simple formulæ ı which they most closely approximate are $CoSi_2$ (48·7% Si) and Co_2Si_5 (54·26% Si). With nickel–silicon alloys the limits of comining power are most widely separated (39—45%); in this case lso a definite compound is not indicated. The upper limit is only ıtained in the presence of at least a 10% excess of free silicon.

The method of analysis consists in the estimation of total silicon y treatment with alkali carbonate and of uncombined silicon by ımoval of the combined element as silicon tetrafluoride by treatıent with pure hydrofluoric acid. Combined silicon is estimated y difference.

The author is led to the conclusion that compounds of the iron roup rich in silicon tend to dissociate partly into free silicon and more or less well-defined compound of silicon and the metal: $_xSi_y \rightleftharpoons M_xSi_{y-z} + Si_z$. Stabilisation occurs in the presence of a ıfficient excess of silicon, but, if this is present in quantity only

sufficient to form the compound, a certain amount of it passes into the free condition (in solution) and so depresses the combining power. H. W.

Form of Ultra microscopic Platinum Particle. RICHARD GANS and RICARDO CALATRONI (*Ann. Physik*, 1920, [iv], **61**, 465—470).—Using platinum sols prepared both by the Bredig process and by reduction of chloroplatinic acid with hydrazine hydrate in the presence of the sodium salt of protalbic acid as protecting colloid, the authors have measured the absorption for the four helium lines λλ 6678, 5877, 5010, and 4472 Å. units. To ensure uniformity of the particles and to remove aggregates, the solutions were filtered through collodion ultra-filters which contained 0·5—1·0% of acetic acid. The results show that as in the case of silver and gold amicrons (A., 1912, ii, 508; 1915, ii, 390), the platinum amicrons are spherical in form (see also Diesselhorst and Freundlich, *Physikal. Zeitsch.*, 1916, **17**, 117). J. F. S.

Mineralogical Chemistry.

The Composition of Coal. The Behaviour of the Constituents of Banded Bituminous Coal on Coking. RUDOLF LESSING (T., 1920, **117**, 247—256).

The Composition of Coal. The Mineral Constituents of Banded Bituminous Coal. RUDOLF LESSING (T., 1920, **117**, 256—265).

Villamaninite, a New Mineral. W. R. SCHOELLER and A. R. POWELL (*Min. Mag.*, 1920, **19**, 14—18).—As black, crystalline grains and small nodules, this occurs disseminated plentifully in a matrix of white, crystalline dolomite, which contains also some iron-pyrites, copper-pyrites, and quartz. It is from the Carmenes mines, near Villamanin, prov. Leon, Spain. Material isolated by dissolving away the dolomite matrix is seen to consist of small groups of rough crystals which show the forms of the cube and octahedron. The cube faces show a peculiar rounding, and it is these faces that form the bright convex and concave surfaces of the nodules. These nodules, never more than sectors of spheres, are due to the subparallel aggregation of crystals. The colour is iron-black with dull metallic lustre, and the streak is sooty-black; H = 4½. The mineral is soluble in nitric acid, leaving a globule of sulphur. Heated in a bulb-tube it gives a sublimate of sulphur and selenium, and it burns in the air with a blue flame. Analysis I is of hand-picked, nodular material; II, of acid-cleaned nodular;

[II, acid-cleaned crystalline; and IV, of acid-cleaned unsorted. Also traces of arsenic, bismuth, lead, and zinc:

	S.	Se.	Cu.	Ni.	Co.	Fe.	SiO_2.	Total.	Sp. gr.
I.	49·00	1·54	17·65	18·19	7·45	4·39	0·88	99·10	—
II.	49·13	1·44	18·51	18·24	7·24	4·17	0·34	99·07	4·433
III.	49·63	0·88	22·13	15·94	6·30	5·11	0·22	100·21	4·523
IV.	47·27	0·88	19·48	15·53	6·79	6·00	3·80	99·75	—

The atomic ratios (S + Se) : (Cu + Ni + Co + Fe) = 1·953, 1·936, and 1·904 for analyses I, II, and III respectively, approximating to the disulphide formula, $(Cu,Ni,Co,Fe)(S,Se)_2$. The presence of copper, nickel, and cobalt in a disulphide is discussed. L. J. S.

The Structure and Symmetry of Anatase, Rutile, Zircon, and Xenotime. A. JOHNSEN (*Centr. Min.*, 1919, 97—105).—Crystals of these minerals have been investigated by the *X*-ray method by Vegard (A., 1916, ii, 405, 593), who came to definite conclusions regarding their inner structure. Vegard's structures have been critically examined by the author, who finds that, whilst those of anatase, rutile, and xenotime are tetragonal holohedral, that of zircon must belong either to the hemimorphous hemihedral or to the hemimorphous tetartohedral class. Experiments on the pyro- and piezo-electric properties of crystals of zircon are desirable to test the point. E. H. R.

Dolomite from Leogang, Salzburg. O. GROSSPIETSCH (*Tsch. Min. Mitt.*, 1917, **34**, 68—70; from *Jahrb. Min.*, 1919, Ref. 274).—Blackish-grey crystals with the form of acute rhombohedra gave:

(CO_2 + trace of S).	FeO.	CaO.	MgO.	Total.	Sp. gr.
47·53	1·63	29·66	21·18	100·00	2·889

The sulphur is due to admixed pyrites. L. J. S.

A Singly Refracting Potassium Aluminium Sulphate of the Alunite Group. E. RAMANN and A. SPRENGEL (*Centr. Min.*, 1919, 35—37).—Among the decomposition products of the rocks of the Solfatara di Puzzuoli, Naples, has been found a potassium aluminium sulphate having the composition

$$K_2O,3Al_2O_3,4SO_4,6H_2O.$$

It seems to have been formed by the action of sulphuric acid on the volcanic rock, and occurs, mixed with sulphur and silica, in the form of very fine particles, 0·001 to 0·002 mm. in diameter. It is singly refracting, but whether it is amorphous or belongs to the regular system it is difficult to say on account of the small size and rounded form of the particles. E. H. R.

Brannerite, a New Uranium Mineral. FRANK L. HESS and ROGER C. WELLS (*J. Franklin Inst.*, 1920, **189**, 225—237).—This is found as grains and rough prisms (tetragonal or orthorhombic?) in gold placers in Stanley Basin, central Idaho. The fragments

have a thin, brownish-yellow crust, but inside the material is bı liant black with conchoidal fracture. Opaque; streak, da greenish-brown; H, 4½. Thin splinters transmit yellowish-gre light, and are optically isotropic; $n_{Li} = 2·26$, $n_{Na} = 2·30 \pm 0·($ D 4·5—5·43; fragments of higher density are more strongly rad active. The mineral is slowly decomposed by concentrated s phuric acid and by hydrofluoric and sulphuric acids. For t analysis it was fused with hydrogen sodium sulphate. Details a given of the method of analysis; titanium and uranium were sep rated by hydrolysis. In determining the state of oxidation of t uranium, the iron was assumed to be all ferrous, and this introdu a difficulty in deducing a formula. Other determinations of ir *gave on unselected material* Fe_2O_3 *3·7%, and on the best select* material Fe_2O_3 3·0 or FeO 2·7%. The least radioactive mater contained TiO_2 35·0%. Analysis by R. C. Wells (also traces $Fe_2($ Al_2O_3, P_2O_5):

SiO_2.	TiO_2.	FeO.	CaO.	UO_2.	UO_3.	ThO_2.	Ce_2O_3.	Yt_2O_3, e
0·6	*39·0*	*2·9*	*2·9*	*10·3*	*33·5*	*4·1*	*nil*	*3·9*

ZrO_2.	PbO.	BaO.	SrO.	H_2O.	CO_2.	Total.	Sp.gr.
0·2	*0·2*	*0·3*	*0·1*	*2·0*	*0·2*	*100·2*	*5·42*

This analysis gives the ratios 9RO, Yt_2O_3, $5RO_2$, $11UO_3$, 46Ti($10H_2O$. Written *as a metatitanate, the formula is*

$$6(Ca,Fe,UO,TiO)TiO_3 + 8(Th,Zr,UO)Ti_2O_6 + Yt_2Ti_3O_9 + 3H_2O.$$

Many analyses of complex uranium minerals are tabulated. Bra nerite contains more uranium than any, with the exception pitchblende. It appears to be nearest delorenzite (A., 1908, ii, 604 but contains less titanium and rare earths. L. J. S.

Crystal Structures of Wulfenite and Scheelite. Rosco G. Dickinson (*J. Amer. Chem. Soc.*, 1920, **42**, 85—93).—Tl *X*-ray spectra of several planes of wulfenite ($PbMoO_4$) and scheeli ($CaWO_4$) have been measured and tabulated. For wulfenite tl following values of n and $\sin \frac{1}{2}\phi_n$ are obtained, together with tl intensities I, plane 101: $n=1$, $\sin \frac{1}{2}\phi_n = 0·0915$, $I=100$; $n=$ $\sin \frac{1}{2}\phi_n = 0·1828$, $I=66$; $n=3$, $\sin \frac{1}{2}\phi_n = 0·2754$, $I=30$; $n=$ $\sin \frac{1}{2}\phi_n = 0·3657$, $I=13$; and $n=5$, $\sin \frac{1}{2}\phi_n = 0·4553$, $I=5$. Measur ments are also made for the planes 100, 110, 001, 111, and 10 In the case of scheelite two sets of values were obtained, usir different specimens, plane 101: $n=1$, $\sin \frac{1}{2}\phi_n = 0·0950$, $I=10($ $n=2$, $\sin \frac{1}{2}\phi_n = 0·1905$, $I=59$; $n=3$, $\sin \frac{1}{2}\phi_n = 0·2860$, $I=18$; $n=$ $\sin \frac{1}{2}\phi_n = 0·3805$, $I=8$. The planes 100, 110, 001, and 111 we also measured. It is shown that the face-centred lattice, with aton so located as to form a diamond arrangement, accounts in each ca for the relative spacings of different planes, and for the densit of the crystals. The arrangement of the heavier atoms relati to one another has been determined by a qualitative consideratic of the relative intensities. The difficulties in the location of tl oxygen atoms are discussed. J. F. S.

[Composition] of Davidite. W. T. COOKE (*Trans. R. Soc. South Australia*, 1916, **40**, 267).—Material from Radium Hill, near Olary, South Australia, gave:

TiO_2.	FeO.	Fe_2O_3.	Ce_2O_3, etc.	U_3O_8.	CaO.	MgO.	PbO.	H_2O.	Total.
54·3	16·0	13·0	8·3	4·6	1·5	0·6	1·1	1·5	100·9

The cerium earths include much Ce, little Th, also La, Di, Er, Yt. Also some V_2O_5 and Cr_2O_3, included with the uranium oxide, trace of copper, and scandium detected spectroscopically. At a red-heat 100 grams of the mineral yielded about 15 c.c. of fairly pure helium. D. MAWSON in a preceding paper (*loc. cit.*, 262—266) describes the mode of occurrence of the mineral, and states it to be homogeneous (compare A., 1910, ii, 309). L. J. S.

Siliceous Sinter from Lustleigh, Devon. A. B. EDGE (*Min. Mag.*, 1920, **19**, 10—13).—Lodes traversing granite and containing a soft and powdery, micaceous hæmatite are worked at the Plumley mine. In one lode, however, this mineral is present as larger scales, and it is cemented into a hard, stony mass by siliceous sinter, which contains also crystals of fluor-apatite, tourmaline, and quartz. The sinter is hard and compact, but very fragile. It ranges in colour from almost pure white to blood-red, with rippled and folded bands of colouring. Analysis of pale red material gave (also CaO, P_2O_5, traces):

SiO_2.	Al_2O_3.	Fe_2O_3.	Na_2O.	K_2O.	H_2O at 105°.	H_2O >105°.	Total.	Sp. gr.
69·76	2·68	5·38	0·36	0·76	18·62	2·38	99·94	1·73

The origin of the material is discussed; it was evidently deposited as a silica jelly. L. J. S.

Hemimorphite on Fossil Bones from Broken Hill, Rhodesia. H. BUTTGENBACH (*Ann. Soc. Géol. Belgique*, 1919, **42**, *Congo Annexe*, 5—14).—Limb bones of mammals from the cave at Broken Hill mine (A., 1908, ii, 397) show (1) compact tissue consisting of calcium phosphate and carbonate with a trace of fluorine, but no chlorine or zinc; (2) a glistening, crystalline crust (anal. I) of hemimorphite coating the compact tissue externally and internally; (3) a spongy aggregate (anal. II) of minute crystals of willemite, smithsonite, hemimorphite, hopeite, parahopeite, and tarbuttite occupying the central cavity.

	ZnO.	Fe_2O_3, Al_2O_3.	CaO.	SiO_2.	P_2O_5.	Ign.	Total.
I.	63·10	1·22	1·68	22·88	1·38	9·30	99·56
II.	45·50	0·82	15·24	15·00	12·75	10·22	99·53

L. J. S.

[Halloysite from Worms Heath, Croydon, Surrey.] GEORGE MACDONALD DAVIES (*Quart. J. Geol. Soc.*, 1920, **75** [for 1919], 22—28).—A petrographical description is given of the

materials (clay, sand, and pebbles) filling large, vertical pipes in the chalk at this locality. A white, clay-like material found in the sand in these pipes, and previously referred to allophane, is proved by the following analysis, by A. B. EDGE, to be halloysite. Formula, $Al_2O_3,2SiO_2,2H_2O+Aq$. Also traces of Na_2O and K_2O. D 2·44; *n* near 1·552. (After ignition, D 2·46 or 2·47; *n* about 1·542.)

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	H_2O (at 100°)	H_2O (100–250°).	H_2O (ign.).	CO_2.	Total.
41·88	36·26	0·30	0·23	7·71	0·85	13·06	0·17	100·46

L. J. S.

The Scapolites. NILS SUNDIUS (*Bull. Geol. Inst. Univ. Upsala*, 1918, **16**, 96—106; from *Jahrb. Min.*, 1919, *Ref.* 140—142).—Supplements previous work (A., 1919, ii, 163). An analysis by Mauzelius (1917) of scapolite from gabbro at Nautanen, Lapland, D 2·698, is calculated as marialite 29·17, sulphate-marialite 9·38, carbonate-meionite 61·46%, and the mineral has the refractive indices ω 1·575, ε 1·552. The composition of carbonate-marialite is now written as $NaHCO_3,3NaAlSi_3O_8$, and of sulphate-marialite as $NaHSO_4,3NaAlSi_3O_8$. Scapolite from lime-silica gneiss in the Gula valley, Trondjem, Norway, gave analysis I (Na_2O,H_2O not determined), corresponding with marialite 6, carbonate-marialite 31, carbonate-meionite 63; it has ω 1·585, ε 1·551.

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Cl.	SO_3.	CO_2.	Total.
I.	48·87	27·55	0·62	15·65	0·18	0·24	—	4·16	97·27

In scapolite from the Laacher See, a redetermination of carbon dioxide in the original material analysed by Brauns (anal. I, A., 1917, ii, 325) gave 3·23% (as against 0·65%), corresponding with marialite 13, sulphate-marialite 10, sulphate-meionite 9, carbonate-meionite 68%; this has ω_{Na} 1·5901, ϵ_{Na} 1·5600. Another, also described by Brauns in 1914, contains CO_2 3·52% (rather than 0·26%), corresponding with marialite 6, carbonate-marialite 31, carbonate-meionite 63, and has $\omega-\epsilon=0·0284$. In their optical constants, these sulphate-rich scapolites do not differ from the carbonate-scapolites, and they fall into the same series.

L. J. S.

Prehnite from the Tatra Mountains. W. PAWLICA (*Bull. Acad. Sci. Cracow*, [*A*], 1916, 54—59; from *Jahrb. Min.*, 1919, *Ref.* 275—276).—Massive, white prehnite with associated epidote, albite, and calcite fills veinlets in oligoclase-biotite-granite on the Mengesdorf peak. In the vicinity of these veins the granite is much decomposed, suggesting that the minerals were deposited by hydrothermal processes. Cavities in the massive mineral are lined with

small crystals of prehnite. The mean of two analyses is (also traces of MnO, MgO, K_2O, Na_2O):

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	H_2O at 110°.	H_2O >110°.	Total.	Sp.gr.
43·89	23·85	1·56	0·28	25·83	0·23	4·52	100·16	2·904

The prehnite is in places altered to a powdery aggregate of sericite scales and quartz grains, being sometimes represented as pseudomorphs. This alteration is expressed as follows:

$3H_2Ca_2Al_2Si_3O_{12}$ (prehnite) + K_2CO_3 + $6H_2CO_3$ =

$2H_2KAl_3Si_3O_{12}$ (sericite) + $3SiO_2$ (quartz) + $6CaCO_3$ + H_2CO_3 + $6HO_2$.

L. J. S.

A New Description of Amesite. EARL V. SHANNON (*Amer. J. Sci.*, 1920, [iv], **49**, 96—98).—A specimen from the disused emery mine at Chester, Massachusetts, shows hexagonal plates 1 cm. across of pale bluish-green amesite, with associated diaspore, magnetite, and rutile. The basal cleavage is not so perfect as in most other chlorites; H $2\frac{1}{2}$, D 2·77. The crystals are optically positive and biaxial, but with very small axial angle; $\alpha=\beta=1{\cdot}597$, $\gamma=1{\cdot}612$. Before the blowpipe, the mineral swells and exfoliates slightly, becoming silvery brownish-white in colour. It is partly decomposed by boiling sulphuric, nitric, or hydrochloric acid, with separation of flocculent silica. Most of the water is lost at only a dull red heat. Analysis:

SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	MnO.	H_2O >110°.	H_2O >110°.	Total.
20·95	35·21	8·28	0·56	22·88	trace	0·23	13·02	101·15

agrees with the formula given by Pisani in 1876, namely,

$$H_4(Mg,Fe)_2Al_2SiO_9,$$

except for the ratio MgO : FeO, which is here = 5 : 1. This formula was adopted by Tschermak in 1890 for a fundamental end-member of the chlorite group. L. J. S.

Optical Characters of the Olivine Group. H. MAGNUSSON (*Geol. För. Förh.*, 1918, **40**, 601—626; from *Jahrb. Min.*, 1919, *Ref.* 277—279).—Previous attempts at the correlation of the optical constants and the chemical composition of the members of the olivine group (A., 1911, ii, 616) have been confined to the series Mg_2SiO_4–Fe_2SiO_4 (forsterite-fayalite). This is now done for the series Mg_2SiO_4–Mn_2SiO_4 (forsterite-tephroite) and Mn_2SiO_4–Fe_2SiO_4 (tephroite-fayalite). Previously published results, supplemented by some new optical determinations, are tabulated and plotted. Passing along the linear series Mg_2SiO_4–Mn_2SiO_4–Fe_2SiO_4, there is a gradual diminution in the optic axial angle and an increase in the refractive indices, but the latter, when plotted against the composition, do not lie along a straight line.

L. J. S.

Belgian Minerals. H. BUTTGENBACH (*Ann. Soc. Géol. Belgique*, 1919, **42**, *Mém.* 93—124).—Crystallographic and optical determinations were made on hopeite, apophyllite, hemimorphite, barytes, anglesite, lepidolite, fuchsite, aragonite, gypsum, and calcite from various localities in Belgium. A brown clay, from Furfooz, with waxy lustre, easily breaking into irregular fragments with conchoidal fracture, unctuous, and adhering to the tongue, has H a little more than 2 and D 2·05. Before the blowpipe it decrepitates, and in the closed tube gives off water and blackens. In water, it breaks up with a slight noise and slowly falls to powder, but does not make a paste. It is, in part, soluble in acids. These characters, as well as the following analysis, point to bole.

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	P_2O_5.	Ign.	Total.
38·67	27·13	11·25	1·15	1·10	1·34	19·34	99·98

The portion (24·21%) soluble in acids contains Al_2O_3 7·67 and Fe_2O_3 9·36%. Deducting these as bauxite ($Al_2O_3,2H_2O$) and limonite, the remainder corresponds in composition with a mixture of halloysite and opal.

A whitish efflorescence on the coal shale of the Bois-l'Evêque colliery, near Liége, is found on optical examination to consist mainly of trona ($3Na_2O,4CO_2,5H_2O$). Recalculating an old analysis (Malaise, 1881) of this material and deducting the sulphate as thenardite or as mirabilite, gives, however, a remainder with the composition $3Na_2O,3CO_2,13H_2O$ or $3Na_2O,3CO_2,11H_2O$.

L. J. S.

The Richardton Meteorite. T. T. QUIRKE (*J. Geol.*, 1919, **27**, 431—449).—This meteorite belongs to the veined spherical chondrite class (Cca) of Brezina's classification. Under the microscope these stones reveal a composition of olivine, monoclinic pyroxene, glass, metallic iron, and troilite. A notable characteristic is the veining. The veins are not continuous, and consist largely of troilite and metallic iron and nickel. In most cases the metal and sulphide are mingled in a manner to suggest contemporaneous deposition or concentration. A few specks of metallic copper were noted in the troilite. An analysis showed: metallic portion 19·90%, silicate portion 80·10%. The metallic portion gave: Fe 90·89, Ni 8·92, Co 0·15, P 0·04%. The silicate portion yielded: SiO_2 44·49, TiO_2 0·10, Al_2O_3 2·46, Cr_2O_3 0·64, Fe_2O_3 4·34, P_2O_5 *none*, MnO 0·19, FeO 16·23, CaO 2·69, MgO 28·32, Na_2O 0·85, K_2O 0·165%. These analyses were made from fragments representative of the matrix, and not on the vein material. It is estimated that about 90 kilos. of material have been recovered, the largest single piece weighing 8·7 kilos.

CHEMICAL ABSTRACTS.

Analytical Chemistry.

A Cheap Substitute for Platinum Wire for Flame Tests. A. EHRINGHAUS (*Centr. Min.*, 1919, 192).—The platinum wire used for carrying out flame tests can be simply and cheaply replaced by a strip of filter paper. To test a solution, a strip of pure filter paper is folded several times, and one end dipped in the solution. The damp end is then held in the outer flame of a Bunsen burner. If an insoluble salt is to be tested, the strip is first dipped in dilute hydrochloric acid, and a little of the salt is then sprinkled on the damp end. In either case, a good, pure flame coloration is obtained, which lasts as long as the paper is prevented from burning by the moisture or the salt. A lasting, monochromatic flame can be obtained by dipping one end of a strip of paper in a vessel containing the dissolved salt, the other end being held in the Bunsen flame. The paper is prevented from burning by a crust of salt, which soon forms. E. H. R.

Use of certain Indicators. Sensitised Sodium Alizarin-sulphonate. W. MESTREZAT (*J. Pharm. Chim.*, 1920 [vii], **21**, 185—192).—Sensitised sodium alizarinsulphonate (prepared by neutralising the commercial product, which is nearly always alkaline in reaction) is a sensitive indicator for use in the titration of mineral acids, oxalic acid, and alkali hydroxides, and possesses the advantage over phenolphthalein and litmus that it can be used for the titration of both ammonia and phosphoric acid; it cannot, however, be used in the presence of carbonates.
W. P. S.

Modified Orsat Apparatus. THOS. B. SMITH (*Gas World*, 1919, **71**, 379).—The gaseous mixture is passed under the maximal pressure of the reservoir through a platinum capillary tube, 13 cm. long and 1·6 mm. in external diameter, which is raised to a white heat, into an additional absorption pipette filled with water. The mixture is thrice returned and re-passed through the capillary, whereby combustible gases are completely burnt. The resultant mixture of carbon dioxide, oxygen, and nitrogen is analysed in the usual manner. CHEMICAL ABSTRACTS.

Improved Method of, and Apparatus for, Detecting Water Vapour or either of the Gaseous Components thereof. HENRY EDWARD FANE GOOLD-ADAMS, WILLIAM HENRY BOUSFIELD, and GEORGE WILLIAM TODD (Brit. Pat. 137547).—The gases suspected of containing water vapour, or either oxygen or hydrogen, which must first be converted into water by passing over a suitable catalyst, are passed over a salt, such as an alkali chloride or nitrate, which forms part of an electric circuit. If the partial pressure of the water vapour exceeds the critical hydration pressure of the particular salt

selected, it takes up moisture and allows a current to pass in the circuit, whereby a suitable indication may be given by means of a galvanometer or an electric bell operated by a relay. The salt is conveniently placed between a pair of wire gauze electrodes, through which the gases are passed. The device is particularly applicable in cases where it is necessary to provide against an explosive mixture of oxygen and hydrogen in gaseous reactions, such as in the synthetic production of ammonia, in which cases a continuous sampling of the mixed gases is secured by means of a by-pass, and a salt is selected of which the hydration pressure is approximately equal to the partial pressure of the aqueous vapour corresponding with the percentage of oxygen, against which a warning is required. G. F. M.

Short Modification of the Official Method of Estimating Chlorine in Foods, Fæces, and Urine. J. O. HALVERSON and E. B. WELLS (*J. Biol. Chem.*, 1920, **41**, 205—208).—The complete washing out of the excess of silver nitrate from the silver chloride precipitate is eliminated, and, instead, an aliquot portion of the direct filtrate is titrated with ammonium thiocyanate. It is recommended that the reagents for titration be 0·05*N*.

J. C. D.

The Oxidation-potentiometric Titration of Iodides in the Presence of Chlorides and Bromides. I. M. KOLTHOFF (*Rec. trav. chim.*, 1920, **39**, 208—214).—Using the method of titration previously described (A., 1919, ii, 352), iodides may be estimated in the presence of any quantity of chlorides or of relatively large amounts of bromides, by titration with potassium dichromate, or, preferably, potassium bromate or iodate, the titration being carried out in the presence of hydrochloric acid.

W. G.

Estimation of Oxygen by the Copper-Ammonia-Ammonium Chloride Reagent. W. L. BADGER (*J. Ind. Eng. Chem.*, 1920, **12**, [2], 161—164).—Hempel's method for the absorption of oxygen by means of metallic copper spirals covered with a solution containing equal parts of saturated ammonium carbonate solution and ammonia (D 0·93) was the basis for a series of experiments in which varying strengths of ammonia, and salts of ammonia other than the carbonate, were used. The results were compared by determining in each case the specific absorption as defined by Anderson. Specific absorptions were found of 22·5 vols. with a concentrated ammonia solution (D 0·90) saturated with ammonium chloride, 45—47 vols. with a mixture of two parts of concentrated ammonia and one of water saturated with ammonium chloride, 55—60 vols. with a mixture of one part of concentrated ammonia and one of water saturated with ammonium chloride, and 30 vols. with a mixture of one part of concentrated ammonia and two of water saturated with ammonium

chloride. The author concludes that an improvement on Hempel's method is obtained by using a solution prepared by saturating a mixture of one part of concentrated ammonia and one of water with ammonium chloride. This solution may be used to absorb fifty to sixty times its volume of oxygen, after which, although its absorption capacity is not exhausted, the amount of precipitate formed makes the solution unworkable. It is claimed that this reagent is cleaner and has a longer life than alkaline pyrogallol; unlike phosphorus, it is unaffected by catalysts, is readily prepared, and is active at almost any temperature. On the other hand, it cannot be used for mixtures containing carbon monoxide or acetylene, and when fresh it is liable to leave measurable amounts of ammonia in the gas. S. S. A.

The Estimation of Nitrogen in Nitrocellulose and Inorganic Nitrates with the Nitrometer. ERNEST GEORGE BECKETT (T., *1920*, **117**, *220—235*).

Estimation of Phosphoric Acid as Ammonium Phosphomolybdate. A. STUTZER (*Landw. Versuchs. Stat.*, 1919, **94**, 251—264).—Conditions are given under which phosphoric acid may be estimated by precipitating it as ammonium phosphomolybdate and weighing the precipitate directly. The precipitation is made in a nitric acid solution containing a small quantity of sulphuric acid, and the precipitate, after being collected on a weighed asbestos filter, is washed first with 2% ammonium nitrate solution, then with alcohol or acetone, dried at 100° for one hour, and weighed. The weight of the precipitate is multiplied by 0·03513 to obtain the amount of P_2O_5. [See, further, *J. Soc. Chem. Ind.*, 1920, 250A.] W. P. S.

Estimation of Arsenic in Organic Compounds such as Salvarsan. L. JOSLYN ROGERS (*Can. Chem. J.*, 1919, **3**, 398).—The sample, 0·5 gram, dissolved in 10 c.c. of water, is treated with 5 c.c. of nitric acid, heated on the hot plate, and solid ammonium persulphate is added until the mixture is colourless; a yellow coloration, if persistent, can be removed by boiling for a few minutes after the addition of a few c.c. of water and several grams of ammonium persulphate all at once. The volume is made up to 100 c.c., 5 c.c. of saturated sodium ammonium hydrogen phosphate solution are added, followed by an excess of magnesia mixture; any precipitate which forms is dissolved by dilute nitric acid. The solution is heated nearly to the b. p., an excess of aqueous ammonia is added, and, after cooling and keeping for two hours, the precipitate is collected, washed with dilute aqueous ammonia, returned, together with the filter, to the precipitation flask, and dissolved in 70 c.c. of dilute hydrochloric acid (three parts of acid to two parts of water). The solution is cooled, shaken for one minute with 3 grams of potassium iodide dissolved in

6 c.c. of water, 70 c.c. of water are then added, and the liberated iodine titrated at once with thiosulphate.

CHEMICAL ABSTRACTS.

Detection of Arsenic in Salvarsan and Neosalvarsan. F. UTZ (*Pharm. Zentr.-h.*, 1920, **61**, 39—42).—The substance is decomposed by heating with a small quantity of sulphuric acid and ammonium persulphate, or with hydrogen peroxide and ferrous sulphate, the solution then diluted, and treated with stannous chloride solution. After a time, the arsenic forms a brown, flocculent precipitate. When a portion of either substance is dissolved in dilute hydrochloric acid in a platinum basin, and a fragment of zinc is added, a brown stain is obtained on the platinum surface. Another test consists in dissolving the substance in concentrated sodium thiosulphate solution and adding hydrochloric acid; sulphur is precipitated, and this is soon coloured bright yellow by the precipitation of arsenic sulphide, which may be separated and identified by the stannous chloride test.

W. P. S.

Renovation of Combustion Tubes. J. DORSMAN (*Chem. Weekblad*, 1920, **17**, 132).—Combustion tubes which have been used for the analysis of substances containing halogens may be renovated as follows. A wash-bottle filled with water is connected to one end of the tube. To the other end an empty U-tube is fitted, connected to a pump. A stream of moist air is drawn through the tube while still red hot. Copper halogen compounds and iodine condense in the cold end and in the U-tube. These may be removed by a piece of wet filter paper. When no further condensation takes place, dry air is drawn through the tube, which is then ready for further use. W. S. M.

Use of Soda-lime in the Calcium Chloride Tube of the Potassium Hydroxide Absorption Apparatus. J. FRIEDRICHS (*Zeitsch. angew. Chem.*, 1919, **32**, 363—364).—Further experiments with gaseous mixtures containing varying proportions of carbon dioxide have confirmed the previous conclusion (this vol., ii, 192) that the use of soda-lime in the calcium chloride tubes of a potassium hydroxide absorption vessel is not only superfluous, but may even be disadvantageous, leading to loss of water. The general belief that potassium hydroxide solution absorbs carbon dioxide less efficiently than soda-lime is probably attributable to the use of absorption apparatus with calcium chloride tubes of insufficient length. The loss of moisture depends on the tension of the absorption agent, the velocity of the gas and the duration of absorption, and is proportional to the last two factors. For the amount of gas evolved in an ordinary elementary analysis, a short calcium chloride tube is sufficient, and no loss of moisture can be observed when the tube is half filled with soda-lime; but in the analysis of carbonates, loss of water is inevitable under such

conditions, and the current of air must be continued for a long time to remove the whole of the carbon dioxide. Similar conditions occur in the estimation of carbon in iron. The dimensions of a calcium chloride tube suitable for this purpose are: length 4 cm. and diameter 0·8 cm. About 1½ grams of calcium chloride are sufficient to dry the gaseous mixture leaving the potassium hydroxide apparatus, provided that this is charged with potassium hydroxide solution (2:3), that the velocity of the gas does not exceed 0·3 c.c. per second, and that the duration of the absorption does not exceed three hours. C. A. M.

Method for the Preparation of a Hydrochloric Acid Solution of Cuprous Chloride for use in Gas Analysis. F. C. Krauskopf and L. H. Purdy (*J. Ind. Eng. Chem.*, 1920, **12**, 158—161).—A solution of stannous chloride was prepared by heating on a sand-bath, to slow boiling, 300 grams of metallic tin contained in a 500 c.c. flask and covered with concentrated hydrochloric acid, a small amount of fresh acid being added from time to time until the solution was saturated with stannous chloride. The solution was then filtered and stored in a flask containing metallic tin to prevent oxidation. A portion of this solution was mixed with cuprous chloride solution and concentrated hydrochloric acid to obtain a solution of cuprous chloride of approximately the same copper and acid content as a corresponding solution of cuprous chloride, free from other salts, prepared by reducing cupric chloride with copper in acid solution. The two solutions were compared by the absorption, in Hempel double pipettes, in the usual way, of carbon monoxide evolved from oxalic acid by the action of sulphuric acid. Figures were obtained which indicate that the efficiency of cuprous chloride solution for the absorption of carbon monoxide is not deleteriously affected by the presence of relatively large amounts of stannous and stannic chlorides; a satisfactory reagent is obtained by reducing cupric chloride in acid solution by means of stannous chloride, and if a small excess of stannous chloride is used, the solution may be exposed to air during transference from one vessel to another without becoming oxidised. Further, the solution may be renewed, after saturation with carbon monoxide, by heating at 60—70° to drive off the gas, a few drops of concentrated stannous chloride solution being added to correct any oxidation which might occur.
S. S. A.

Estimation of Carbon Dioxide, Oxygen, and Combustible Gases by Krogh's Method of Micro-analysis. Hans Oluf Schmit-Jensen (*Biochem. J.*, 1920, **14**, 4—24).—It is shown that Krogh's micro-gas analysis apparatus may be used to estimate hydrogen and carbon monoxide in very small gas samples (*Skand. Arch. Physiol.*, 1908, **20**, 279). As absorbent for hydrogen, a solution of 0·66 gram of colloidal palladium and 0·42 gram of sodium picrate in 20 grams of distilled water is used, and as

absorbent for carbon monoxide an acid solution of cuprous chlorid A modification of Krogh's apparatus is described by means which it is possible to estimate carbon dioxide and oxygen b absorption, hydrogen and methane by combustion, and carbo monoxide either by absorption or combustion. The hydrogen ar methane can only be estimated by combustion if the bubble of g has a volume of at least 80 cu. mm.; nitrogen is also taken b difference. The fractional combustion of hydrogen and metha is also possible by means of this apparatus. The average error the readings is about ±0·1 mm. This systematic error is differe with the different gases, and in the case of oxygen, hydroge methane, and carbon dioxide is of no practical importance, but must be taken into consideration with carbon dioxide. A sma receiver for collecting gas samples is described. J. F. S.

Direct Estimation of Potassium and Sodium in Sma Quantities of Blood. B. KRAMER (*J. Biol. Chem.*, 1920, **41** 263—274).—The method for potassium is a modification of th sodium cobaltinitrite method capable of being used for 1 c.c. blood or 3—5 c.c. of plasma or serum. The sodium proce is based on the precipitation of that element as the pyroant monate, which is weighed as such. The potassium content normal human serum varies between 16 and 22 mg. per 100 c. of serum. The sodium content has been found in both norm children and adults to vary between 280 and 310 mg. per 100 c. of serum. J. C. D.

Estimation of Zinc in Organic Materials, such as Food Urine, and Excrement. The Zinc Content of Reagent and Analytical Vessels. A. WEITZEL (*Arb. Gesundh. Amt* 1919, **51**, 476—493; from *Chem. Zentr.*, 1920, ii, 5—6).—Tw methods are described for the estimation of zinc in organic sub stances. In the first of these, the material is converted into ash either by the wet or dry process; the latter is dissolved in acid copper, etc., is removed by hydrogen sulphide, and zinc is pre cipitated from the acid filtrate by potassium ferrocyanide. Th zinc ferrocyanide is decomposed by concentrated sulphuric acid zinc is precipitated in the usual manner with ammonium sulphide the precipitate is dissolved in hydrochloric acid, and the zinc i again precipitated by hydrogen sulphide from acetic acid solution The sulphide is finally dissolved in 1% hydrochloric acid, the zin is precipitated with sodium carbonate, and weighed as the oxide The second method is identical with the first as far as the separ ation of sulphides of copper, etc. Ferrous compounds are the oxidised by nitric acid, sodium hydroxide is added, and the dis turbing effect of phosphates is overcome by acidification with aceti acid. The residue left on filtration is separated as completely a possible from the mother liquor and dissolved in dilute hydro chloric acid; it is again treated with sodium hydroxide and aceti acid, and, if necessary, the process is repeated until zinc can n

onger be detected in the acid filtrate by means of potassium ferro-yanide. The united acetic acid filtrates are saturated with ıydrogen sulphide. The details of the two methods are minutely lescribed in the original. Either process permits an exact estim-tion of zinc as oxide in urine, excrement, animal organs and issues, and in foods, even if the metal is only present in minimal mounts. It is a matter of indifference whether the organic aterial is oxidised by the wet or dry process. The second method s to be preferred to the potassium ferrocyanide process, since it equires a smaller number and smaller amounts of reagents, and an be carried out in a shorter time. If the directions are closely ollowed, and pure reagents free from zinc are used, so little zinc asses into the material under investigation, either from the eagents or from the Jena-glass flasks, which contain considerable uantities of zinc, that it need not be taken into account even for he most accurate analyses. Otherwise, in those cases in which oncentrated solutions of alkali hydroxide or phosphoric acid are oiled, or even small quantities of fluorides are warmed with ıineral acids in vessels made of glass containing zinc, the possi-ility of the passage of zinc from the vessel into the material nder investigation must always be taken into account; in these ircumstances, the use of vessels made of glass free from zinc is dvisable. H. W.

Estimation of Mercury in Organic Combination by ıeans of Zinc Filings. MAURICE FRANÇOIS (*J. Pharm. Chim.*, 920, [vii], **21**, 85—91).—A modification of a method described reviously (A., 1918, ii, 276) is recommended. The substance is issolved by heating with alcohol, and the solution is then treated ith hydrochloric acid and zinc filings. With mercury benzoate nd mercury salicylate, the reduction with zinc is carried out in odium hydroxide solution containing potassium iodide, and any xcess of zinc is dissolved subsequently by treatment with hydro-hloric acid. W. P. S.

Estimation of Iron in Iron Ores by means of Perman-anate. L. BRANDT (*Chem. Zeit.*, 1920, **44**, 101—103, 121—122).—ompare A., 1919, ii, 373, 480).—A further criticism of the method escribed by Schwarz and Rolfes (A., 1919, ii, 170). W. P. S.

The Analysis of Wulfenite Earths from Mies. E. DITTLER *Centr. Min.*, 1919, 225—227).—A method has been devised by hich calcium, lead, molybdenum, and zinc can be estimated in a ngle sample of the mineral. About a gram of the finely powdered aterial is digested successively with hydrochloric and nitric acid ıtil the residue is no longer black. Digestion is then continued ith sulphuric acid to convert the calcium and lead into sulphates, ıd the solution is diluted and filtered, the residue being washed veral times with dilute sulphuric acid. The residue is then xtracted with ammonium acetate solution, which dissolves both

calcium and lead. These are again precipitated as sulphates, weighed in a Neubauer platinum crucible, then dissolved in hydrochloric acid, the calcium precipitated as oxalate, and the lead estimated by difference. The acid solution containing the molybdenum and zinc is neutralised with ammonia, the iron present precipitated by addition of ammonium chloride and filtered, the solution made strongly ammoniacal, and saturated with hydrogen sulphide. The zinc sulphide is then salted out by addition of ammonium thiocyanate, and the molybdenum determined in the filtrate by known methods. E. H. R.

Separation of Zirconium and Titanium as the Phosphates. JAMES BROWN and H. T. MADDEN (*J. Amer. Chem. Soc.*, 1920, **42**, 36—39).—Zirconium and titanium may be separated and estimated by the following method. The solution, containing 1—2% by volume of sulphuric acid, is treated with an excess of hydrogen peroxide, and then with an excess of disodium or diammonium phosphate, and the solution kept overnight. The precipitated zirconium phosphate is collected and washed with water containing a few drops of sulphuric acid and a little hydrogen peroxide. If, as is usually the case, the precipitate is coloured yellow by titanium, it is fused with sodium carbonate, extracted with water, and redissolved by fusing with potassium hydrogen sulphate, and then treating with dilute sulphuric acid. The zirconium is then reprecipitated as above, and if the precipitate is colourless, all the titanium has been removed. The zirconium phosphate is now converted into oxide by fusing with sodium carbonate, extracting with water, dissolving the residue in hydrochloric acid, and precipitating with ammonia. The precipitate is washed, dried, ignited, and weighed as the dioxide. The combined filtrates from the zirconium precipitation are boiled to decompose hydrogen peroxide, and the acidity adjusted so that the content of sulphuric acid is about 2% by volume. An excess of disodium or diammonium phosphate is added, the mixture kept for one hour, and then filtered. The precipitate of titanium phosphate is washed, converted into the dioxide, as in the case of zirconium, and weighed. The results given in the paper show that the method is capable of a high degree of accuracy. J. F. S.

Testing of Chloroform. F. UTZ (*Pharm. Zentr.-h.*, 1917, **58**, 1—5).—The author has investigated, in particular, the benzidine test for the detection of decomposition products in chloroform. When benzidine is dissolved in pure chloroform, the solution remains unchanged for twenty-four hours if kept in a dark place; if chloral is present, a faint red coloration develops at first, and changes to bluish-red after a time. A turbidity forms immediately if the chloroform contains carbonyl chloride, hydrochloric acid, or chlorine, and a flocculent precipitate may separate. W. P. S.

The Reduction of Aromatic Nitro-compounds by Stannous Chloride and by Titanous Chloride, and their Volumetric Estimation. DANIEL FLORENTIN and HENRI VANDENBERGHE (*Bull. Soc. chim.*, 1920, [iv], **27**, 158—166).—The estimation of nitro-groups by reduction with stannous chloride and titration of the excess of the latter with iodine solution in neutral or acid medium (compare Altmann, A., 1901, ii, 475; Druce, A., 1919, ii, 199), gives satisfactory results with nitrobenzene and various di- and tri-nitro-derivatives, but, contrary to the results obtained by Druce (*loc. cit.*), the authors find that the results obtained for the mononitrotoluenes are too low, owing to the formation of *p*-chlorotoluidines.

Titanous chloride quantitatively reduces the nitro-compounds according to the equation $C_6H_5 \cdot NO_2 + 6TiCl_3 + 6HCl = C_6H_5 \cdot NH_2 + 6TiCl_4 + 2H_2O$, except in the case of *o*-nitrotoluene, which gives results which are about 3% too low. The excess of titanous chloride *is determined by titrating it into a known volume of standard* ferric sulphate solution, using ammonium thiocyanate as an indicator. W. G.

Differentiation of Methyl and Ethyl Alcohols. TH. SABALITSCHKA (*Pharm. Zentr.-h.*, 1920, **61**, 78—79).—Although the copper sulphate test (compare Pannwitz, this vol., ii, 62) has a limited use for the detection of methyl alcohol in ethyl alcohol in the absence of water, it is untrustworthy in the case of dilute alcohols. W. P. S.

The Estimation of Incompletely Nitrated Phenol in the Mother Liquors from Picric Acid by means of Bromine. M. MARQUEYROL and P. CARRÉ (*Bull. Soc. chim.*, 1920, [iv], **27**, 127—138).—The results obtained by Jolibois's method, by the action of bromine on the incompletely nitrated phenol in the mother liquors from picric acid are inaccurate and variable. The results obtained are too high, and vary with the time and temperature of contact of the bromine with the mother liquors and the amount of bromine in excess. It is shown that these mother liquors contain a mixture of sodium 2:4-dinitrophenol-*o*-sulphonate and sodium 2:6-dinitrophenol-*p*-sulphonate in variable proportions, together with some sodium nitrophenolsulphonate. The action of the bromine on each of the dinitrophenolsulphonates varies with the conditions given above; the mononitrophenolsulphonates tend to give dibromo-derivatives, and any picric acid remaining in the mother liquors is acted on by the bromine, all of these changes tending to vitiate the results obtained by Jolibois's method. W. G.

The Estimation of Incompletely Nitrated Phenol in the Mother Liquors from Picric Acid; the Ratio between the Composition of these Mother Liquors and the Yield of a Manufacture of Picric Acid. M. MARQUEYROL and P. CARRÉ (*Bull. Soc. chim.*, 1920, [iv], **27**, 138—140).—Marqueyrol and

Loriette's method is slightly modified. The mother liquors are completely nitrated, and the resulting picric acid is collected and estimated volumetrically by titration with $N/10$-sodium hydroxide. It is necessary to apply a correction for the amount of picric acid dissolved in the water with which the precipitate is washed. [See, further, *J. Soc. Chem. Ind.*, 1920, 248A.]

W. G.

Estimation of Traces of ββ′-Dichloroethyl Sulphide [Mustard Gas] in Air. MAX YABLIK, G. ST. J. PERROTT, and N. H. FURMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 266—274).—The method is based on the observation that a solution of selenious acid in sulphuric acid (1 : 1) is reduced by traces of ββ′-dichloroethyl sulphide, giving an orange-red suspension of selenium; the presence of about 0·005 mg. of dichloroethyl sulphide can be detected in this manner. The estimation of the vapour in air is effected by bubbling the mixture through a suitable absorbent, such as a 1% solution of seleninm dioxide in water, adding 10 c.c. of a solution of selenious acid in sulphuric acid, care being taken to use the latter in such a manner that a 1 : 1 solution is finally obtained, and also that the concentration of selenious acid in the ultimate mixture is the same as in the absorbing mixture. The solution is then heated for ten minutes in a bath at 85°, cooled, and the strength estimated by nephelometric comparison with standard solutions prepared from weighed quantities of the reageuts. The process is available for amounts of substance between 0·1 mg. and 0·01 mg., with a maximum error of 0·005 mg. The temperature at which the solution is heated in process of "developing" can vary 5° in either direction without affecting the character of the suspension. The method is remarkably free from the necessity for extreme purity of original solution, cleanliness of glassware, etc., which obtains in silver haloid nephelometry. It was not found possible to nse good solvents for dichloroethyl sulphide as absorbing media, and then determine the strength of the solutions by the proposed method, since the only suitable solvent (alcohol and acetic acid) reduced the selenious acid to some extent. The selenious reagent is not specific to mustard gas; arsine and the substitnted arsines, and several other toxic gases, react with it vigorously.

Attempts to determine the strength of the suspension colorimetrically were not successful.

H. W.

The Nephelometric Values of Cholesterol and the Higher Fatty Acids. II. F. A. CSONKA (*J. Biol. Chem.*, 1920, **41**, 243—249).—The nephelometric values of oleic acid and cholesterol were found to be influenced by the hydrolysis, as well as by the addition of certain substances which alone, in similar circumstances, do not produce any turbidity. These influencing agents are exemplified by the use of gelatin as a protective colloid.

J. C. D.

Formation of β-Methylumbelliferone as a Reaction of Acetoacetic Acid and its Esters. VICTOR ARREGUINE and EDOUARD D. GARCIA (*Ann. Chim. anal.*, 1920, [ii], **2**, 36—41, *Anal. Soc. Quim. Argentina*, 1919, **7**, 424—432).—In hydrochloric acid solution, acetoacetic acid condenses with resorcinol to form β-methylumbelliferone, and the latter exhibits an intense blue fluorescence when the solution is rendered slightly ammoniacal. To make the test, 2 c.c. of hydrochloric acid containing a trace of acetoacetic acid or ethyl acetoacetate and 0·1 gram of resorcinol are boiled for a few minutes, cooled, diluted with water, and treated with a slight excess of ammonia. In the case of urine, 50 c.c. of the sample are treated with three drops of hydrochloric acid and extracted first with 5 c.c. and then with 3 c.c. of carbon tetrachloride; the latter solution is evaporated to about 3 c.c., and then tested as described. The test will detect 0·00002 gram of acetoacetic acid in 5 c.c. of urine. The reaction is specific, and is not given by acetone or β-hydroxybutyric acid.

W. P. S.

Estimation of Acetone and Acetoacetic Acid with Autenreith's Colorimeter. EMIL LENK (*Münch. med. Woch.*, 1919, **66**, 1119—1120; from *Chem. Zentr.*, 1919, iv, 995).—A reply to Schall (this vol., ii, 63), in which it is pointed out that the latter has simply adopted the author's method with the substitution of Autenreith's colorimeter for a measuring cylinder.

H. W.

Analysis of Acetone by Messinger's Method. LEO FRANK GOODWIN (*J. Amer. Chem. Soc.*, 1920, **42**, 39—45).—Messinger's method for the analysis of acetone (A., 1889, 313) has been critically investigated. The method consists in shaking acetone in the presence of alkali hydroxide with an excess of iodine. After ten minutes, the solution is acidified, and the excess of iodine titrated with a standard solution of sodium thiosulphate. It is shown that under proper conditions the method gives accurate and concordant results. The effect of keeping, the method of shaking and adding the iodine solution, the effect of an excess of acid, and the dilution have all been investigated and found to be without influence on the results. It is shown that methyl and ethyl alcohol if present both use up a certain amount of iodine. J. F. S.

The Acetone Concentration in Blood, Urine, and Alveolar Air. I. A Micro-method for the Estimation of Acetone in Blood, Based on the Iodoform Method. ERIK MATTEO PROCHET WIDMARK (*Biochem. J.*, 1919, **13**, 430—445).—The blood is drawn from the finger or ear lobe into a capillary pipette graduated to 100 c.mm., and is then transferred into the flask of the distillation apparatus, in which there has previously been placed 10 c.c. of 1% phosphoric acid. The pipette is washed out several times with the acid. The distillation must be carried out within two or three hours of the drawing of the blood, and the distillate is collected in a cooled test-tube containing 3 c.c. of

N/2-sodium hydroxide and 2 c.c. of *N*/200- or *N*/100-iodine solution, according to the amount of acetone. The residual iodine is titrated with equivalent sodium thiosulphate after the contents of the tube have been treated with 3·5 c.c. of *N*/2-sulphuric acid. The presence of ethyl alcohol in the blood has no effect on the results of the titration. As a micro-method, the process is not applicable to normal blood and urine, but gives trustworthy results in pathological conditions where there is an increased amount of acetone in these fluids. J. C. D.

Estimation of Acetone Substances. N. O. ENGFELDT (*Acta med. scand.*, 1919, **52**, 311—366; from *Chem. Zentr.*, 1920, ii, 161—162).—Salén's proposed modification (*Nord. med. ark. avd.*, 1918, ii, **51**, No. 11) of the author's previous method for the estimation of acetone substances in urine is unsatisfactory, since errors of 24·5—41·5% occur. Recent investigations lead to a modification of the method, which is now carried out in the following manner. Precipitation of the urine is effected with ammonia, lead acetate, and alum in an exactly specified manner, and, after dilution and acidification with concentrated sulphuric acid, the acetone is distilled and the distillate is titrated with iodine. Chromate and sulphuric acid are added, and the residue is again distilled; the iodine required is a measure of the β-hydroxybutyric acid. Another estimation, in which, first, concentrated sulphuric acid, and then, shortly afterwards, chromate and sulphuric acid are added, permits the measurement of the total acetone substances of the urine as acetoacetic or β-hydroxybutyric acid by one distillation which can be performed in twenty-five minutes. It should be noted that the presence of alcohol in urine, arising from fermentation of dextrose or imbibed by the patient, disturbs the estimation. Toluene, which is more soluble in urine than in distilled water, is, in 2·5% concentration, an active disinfectant, and is recommended as a preservative, since it does not interfere with the estimation.

The author has elaborated a somewhat similar clinical method for the estimation of acetone substances in blood, the details of which will be published shortly. H. W.

Estimation of Dextrose in the Presence of Lactose. E. HILDT (*J. Pharm. Chim.*, 1920, [vii], **21**, 136—137; *Ann. Chim. anal.*, 1920, [ii], **2**, 78—80; *Ann. Falsif.*, 1920, **13**, 21—25).—A Fehling's solution is used, 10 c.c. of which correspond with 0·048 gram of dextrose and 0·071 gram of lactose hydrate or 0·051 gram of lactose after hydrolysis. The solution containing the two sugars is titrated direct into 10 c.c. of the Fehling's solution, and again after hydrolysis. For the hydrolysis, an amount of the sugar solution containing not more than 1 gram of lactose is heated for six hours at 95—98° with 20 c.c. of an 18% solution of sodium benzenesulphonate in *N*-sulphuric acid, after making the mixture up to 100 c.c. with distilled water. W. G.

Estimation of Sugar in Diabetic Blood. G. VIGEVANI (*Boll. Chim. farm.*, 1919, **58**, 436—439).—Two c.c. of the blood are mixed with 100 c.c. of potassium chloride solution (saturated potassium chloride solution 340 c.c., hydrochloric acid 0·375 c.c., and water 160 c.c.), 50 c.c. of the mixture boiled for five minutes, filtered from the precipitated proteins, the filtrate made up to definite volume, and 10 c.c. introduced into an Erlenmeyer flask, round the neck of which rubber tubing has been fixed. From 1 to 2 c.c. (according to the amount of dextrose) of a copper solution (copper sulphate 2·2, potassium hydrogen carbonate 80, potassium carbonate 50, potassium chloride 53 grams; water, 500 c.c.) are added, the mixture boiled for three minutes, and the rubber tube closed with a clip, so that a vacuum is produced within the flask after cooling. A current of carbon dioxide is then introduced, and the liquid titrated with iodine solution (N/10-hydrochloric acid 5 c.c., iodine 0·0635 gram, potassium iodide 2 grams, 2% potassium iodate solution 2 c.c., and water to 100 c.c.), with starch solution (2 grams of soluble starch in 100 grams of saturated potassium chloride solution) as indicator. The copper reduced by the dextrose reacts with the iodine solution. The latter is previously standardised on pure dextrose which has been dried at 100°. C. A. M.

Method of Identification of Amino-acids. SHINTARO KODAMA (*J. Tokyo Chem. Soc.*, 1919, **40**, 743—754).—The principle of the method, which in this paper deals only with phenylalanine, consists in converting the amino-acid into the hydroxy-acid and determining the m. p. of the latter.

A solution of 0·2—0·3 gram of phenylalanine in a slight excess of acid (preferably sulphuric acid) is treated at 80° with a solution of sodium nitrite very slowly until nitrogen ceases to be evolved. The solution is boiled for two to three minutes, diluted with water to twice or thrice its volume, boiled with calcium carbonate for twenty to thirty minutes, filtered, and concentrated to 5—7 c.c. Calcium phenyl-lactate is precipitated by the addition of a few drops of 2M-calcium chloride. The phenyl-lactate is dissolved in 2 c.c. of concentrated hydrochloric acid, and the m. p. of the phenyl-lactic acid which separates after several hours is determined after recrystallisation from alcohol or benzene.

The author has isolated another hydroxy-acid, m. p. 93—94°, mol. wt. 176, which is very strongly lævorotatory, and is probably derived from an isomeride of phenylalanine.

The phenylacetaldehyde obtained by heating 0·01 gram of phenyl-lactic acid develops with 2—3 c.c. of 50% alcoholic sulphuric acid a permanent, green coloration after keeping for several hours.

CHEMICAL ABSTRACTS.

Detection of Carbamide. J. F. A. POOL (*Pharm. Weekblad*, 1920, **57**, 178—179).—The presence of the enzyme urease may be detected in soja beans by means of the colour effects produced in a jelly containing 2% of carbamide and aqueous yeast extract (A.,

1916, i, 536). Conversely, the presence of carbamide in solution may be shown by making the liquid neutral to phenolphthalein adding 2% of agar-agar, boiling, and placing a small section of soja bean on a portion of the jelly solidified in a watch-glass. After some time a red coloration begins to spread from the bean outwards. W. S. M.

Method of Estimating Quinine and Strychnine when Occurring in Common Solution. A. R. Bliss (*J. Amer. Pharm. Assoc.*, 1919, **8**, 804—807).—The method is based on the solubility of strychnine in water (1 in 6420) and its slight solubility in ethyl ether. Fifty c.c. of the preparation are freed from alcohol a slight excess of citric acid is added, followed by an excess of aqueous ammonia, the total alkaloids are extracted by chloroform-ether mixture, the extract is evaporated, and the residue is dried and weighed. The total alkaloids are dissolved in dilute sulphuric acid, an excess of water (more than 6500 times the weight of the strychnine) is added, together with an excess of aqueous ammonia and the mixture is shaken seven times with ether. The ethereal extracts are united, washed with 5 c.c. of water and evaporated and the residue is dried and weighed as quinine. The residual aqueous solution is extracted seven times with chloroform, the extracts are united and evaporated, and the residue is dried and weighed as strychnine. Excellent results are recorded for solutions of approximately known strength. Chemical Abstracts.

A Modification of the Francis-Connell Method of Estimating Hydrocyanic Acid. Paul Menaul and C. T. Dowell (*J. Agric. Res.*, 1920, **18**, 447—450).—See this vol. i, 359.

The Toxicological Detection of Physostigmine [Eserine]. H. Fühner (*Biochem. Zeitsch.*, 1918, **92**, 347—355).—Quantities of 5/1000—1/100 mg. of eserine can be detected by means of the biological eye reaction in the cat. The author finds that in the case of the plain muscle of the leech, minute quantities of eserine in the presence of acetylcholine increase the contraction of the muscle brought about only to a small extent by acetylcholine alone. By this joint action of the two drugs on the muscle of the leech 1/10,000 mg. of eserine can be detected with certainty. S. S. Z.

A Quantitative Biological Method for the Estimation of Nicotine. H. Fühner (*Biochem. Zeitsch.*, 1918, **92**, 355—364). —By means of the contraction produced by the action of nicotine on the plain muscle of the leech, it is possible to estimate quantitatively 1/100 mg. of the drug. The myograph of the nicotine solution of unknown strength is compared with that of a solution of known strength. S. S. Z.

General and Physical Chemistry.

Perturbation Theory of the Helium Atom. A. LANDÉ (*Physikal. Zeitsch.*, 1920, **21**, 114—122).—A purely mathematical paper, deducing the series spectra of helium by the consistent application of the quantum theory to a system of two electrons revolving round a nucleus of charge $+2e$ in circular and elliptical paths, co-planar and inclined. F. S.

The K-Absorption Bands of Rare Earths for X-Rays. M. DE BROGLIE (*Compt. rend.*, 1920, **170**, 725).—The author has obtained the K bands for the elements numbered 69, 70, 71. The band of lutecium is placed between the two groups K_α and K_β of tungsten. Approximate measurements give the K band of thulium ($N=69$) at $\lambda=0{\cdot}208\times10^{-8}$, of neoytterbium ($N=70$) at $\lambda=0{\cdot}2015\times10^{-8}$, and of lutecium ($N=71$) at $\lambda=0{\cdot}195\times10^{-8}$. W. G.

The Constitution of Atmospheric Neon. F. W. ASTON (*Phil. Mag.*, 1920, [vi], **39**, 449—455).—The observation in 1912 by Sir J. J. Thomson of a faint but unmistakable parabola corresponding roughly with an atomic weight 22, in addition to the expected one at 20, in the positive ray spectrum of neon, and the absence of any parabola at 22 except in presence of neon, was strong evidence of the line being due to an isotope of neon. Fractional distillation failed to effect any separation, and diffusion results, although more hopeful, have failed to be conclusive. A difference of 0·7% in density in the first set of experiments could not be repeated in more elaborate ones, 0·3% difference only being obtained. By new and refined methods of positive-ray analysis, exact measurements have shown that the atomic weight of the two constituents in neither case corresponds exactly with that of neon, 20·2. Four parabolas corresponding with the doubly and singly positively charged atoms of the two isotopes have been carefully measured. The corrected results gave for the one constituent (Ne^{α}) an atomic weight of 20·00, and for the other (Ne^{β}) 22·00, to an accuracy of about 0·1%. The intensities of the lines were in agreement with the required 90% to 10% ratio. On the clearest spectra there was evidence of a third isotope of mass 21, extremely faint, and probably not present to the extent of 1%. F. S.

Radioactive Disintegration Products in the Free Atmosphere and the Probability of their Origin being the Sun. HERMANN BONGARDS (*Physikal. Zeitsch.*, 1920, **21**, 141—145).—The radioactivity of a wire suspended at a mean height of 1500 metres, under the influence of the earth's field, has been determined. It is shown that a relationship exists between the activity,

the air pressure at the earth's surface, and the potential tempe ture in the air layer between 1000 and 2500 metres. A we defined parallelism is observed between the activity and t temperature in this air layer. The temperature changes a regarded as the cause of the pressure changes. Since the influen of the radioactive substances on the temperature cannot occur the observed extent, and since temperature is without influence the activity, it is assumed that a radiation of material from definite and restricted portion of the sun is the cause of t observed effects. This radiated matter carries with it the ema ation particles which are observed in the atmosphere. The he action of the material radiations constitutes the chief source heat of the higher layers of the atmosphere. J. F. S.

Intermolecular Change of Place of Similar Atom GEORG VON HEVESY and LÁSZLÓ ZECHMEISTER (*Ber.*, 1920, 5 [*B*], 410—415. Compare von Hevesy and Rona, A., 1915, ii, 24 —By employing radioactive methods, the authors show that inte molecular change of place occurs between lead atoms to an exte which can be exactly calculated from the law of probabili when they are in an ionised state; organically combined le atoms are not subject to similar transposition in homogeneo phase. Thus, when activated lead nitrate and inactive le chloride are dissolved in molar proportions in boiling pyridine, a the solution is kept hot for some time and then allowed to co the lead chloride which separates is found to be exactly half radioactive as the original specimen of lead nitrate. Simil results are obtained with the following pairs of compounds: le formate (active) and lead acetate in water; plumbous aceta (active) and plumbic acetate in glacial acetic acid; plumbic aceta (active) and plumbous acetate in glacial acetic acid. Interchan does not occur with lead chloride (active) and lead tetraphenyl pyridine, with lead acetate (active) and lead tetraphenyl in am alcohol, or with lead nitrate (active) and lead diphenyl nitrate dilute ethyl alcohol. H. W.

Radioactivity of the Rocks of the Kolar Gold Field HERBERT EDMESTON WATSON and GOSTABEHARI PAL (*J. Ind. In Sci.*, 1914, **1**, 39—46).—The Kolar goldfields on the Myso plateau are worked to a depth of 1100 m., and the rock consis of schists of very uniform character. The rocks were fused wi potassium hydroxide in a copper flask under reduced pressure, a the radium emanation found to be liberated as completely as the higher temperature required for fusion with alkali carbonate Some nearly pure hydrogen is liberated, which causes the readin in the electroscope to be low, and it was eliminated by passi the gas over red-hot copper oxide before introducing it in the electroscope. The mean quantity of radium in the schists w found to be 0·19 [$\times 10^{-12}$ gram of radium per gram of rock], t quantity varying but little with depth. These rocks, which a

probably the oldest known, contain as little radium as any yet examined, and the temperature gradient in the mines is abnormally small. Other specimens of rocks of later date contained larger amounts of radium, from 0·8 to 6·9. F. S.

Radioactivity and Life. H. Zwaardemaker (*Arch. Néerland. Physiol.*, 1920, **4**, 177—196).—A general discussion of work already published (compare A., 1917, i, 241; 1918, i, 326; ii, 182). W. G.

The Cathode Fall. I. In Neon and Helium. H. E. Watson and G. R. Paranjpé (*J. Ind. Inst. Sci.*, 1918, **2**, 143—165).—From Aston's results (*Proc. Roy. Soc.*, 1911, **84**, 526), the cathode fall should be equal to the total difference of potential across the electrodes when the anode is situated in the negative glow. A systematic investigation has been made of the requirements necessary to obtain trustworthy results by this method. Using a cylindrical tube with plane parallel electrodes 7·2 cm. in diameter, the same diameter as the tube, the minimum cathode fall was found to be constant to 1 volt over a wide range of pressure—185 volts between 6 and 16 mm. for copper electrodes in neon—while the current was passing. The laws governing the relations between the cathode fall, the gas pressure, and the current were found to agree with those found by other observers using exploring wires. The cathode fall was determined in very pure helium and neon for twenty-four different metals as cathodes, and with few exceptions were all within 5% of 145·5 volts for neon and 155·5 for helium. F. S.

The Cathode Fall. II. In Argon, Hydrogen, and Nitrogen. Gopal Paranjpé (*J. Ind. Inst. Sci.*, 1918, **2**, 166—177).—The cathode fall for twenty different metals in argon, nitrogen, and hydrogen has been determined, and in any one gas found to be nearly, but not exactly, the same for all metals. The differences in different gases for the same metal were nearly all independent of the metal, but the results in hydrogen were irregular. Nitrogen behaved very similarly to the monatomic gases. F. S.

Electrical Conductivity in Solid Crystallised Compounds. I. Verification of Faraday's Law in the Electrolysis of Solid Salts of Heavy Metals. C. Tubandt and Sophie Eggert (*Zeitsch. anorg. Chem.*, 1920, **110**, 196—236).—One of the most important difficulties encountered in the practical determination of the conductivity of solid salts and the verification of Faraday's law for such conductors is the short-circuiting brought about by the formation of a bridge of metal, formed by the electrolysis of the salt, between the anode and the cathode. The metal is deposited in the form of very fine threads or delicate, dendritic growths, which spread so rapidly across the electrodes that a

quantitative investigation of the electrolysis of the salt is impossible. It has been found that the cubic form of silver iodide, when electrolysed, using a silver anode and a platinum cathode, gives a deposit of silver at the cathode in the form of a perfectly coherent tree, the growth of which is so slow that there is no danger of short-circuiting. The hexagonal modification of silver iodide, stable below 144·6°, has a maximum specific conductivity of 0·00034, whilst the cubic modification has at the transition point the much greater value 1·31, which rises to 2·64 in the neighbourhood of the melting point, 552°. By carrying out the electrolysis of the salt at about 150°, using a current of 0·04 to 0·1 amp., a complete verification of Faraday's law was obtained, both the loss of silver from the anode and the weight deposited at the cathode agreeing within a fraction of 1% with the weight of silver deposited in a silver voltameter included in the circuit. The law was also verified for silver bromide, chloride, and nitrate by interposing a layer of silver iodide between the cathode and the salt under examination, the iodide ensuring that the metal was deposited at the cathode in a coherent form. The electrolysis of lead chloride, bromide, and iodide was also investigated, using a silver anode and a platinum cathode. The loss of silver from the anode afforded a complete verification of the law, but owing to the dendritic form in which the lead was deposited at the cathode, no trustworthy results could be obtained from this side. In choosing the temperature at which to carry out the electrolysis, care had to be taken that no fusion occurred, and for this purpose the fusion diagrams for the systems $PbCl_2$–AgCl, $PbBr_2$–AgBr, and PbI_2–AgI were investigated experimentally. Silver and lead chlorides form a eutectic at 314°, containing 40 mols. % of lead chloride. Silver and lead bromides form a compound,

$$2PbBr_2,AgBr;$$

there are two eutectic points, the first at 276° with 46 mols. % of $PbBr_2$, this eutectic crystallising from mixtures containing 0—66·67 mols. % of $PbBr_2$, all other mixtures showing eutectic crystallisation at 295°. Silver iodide–lead iodide mixtures show eutectic crystallisation at 395° with 0—20 mols. % AgI. From this point up to 100% AgI, mixed crystals of the compound $4AgI,PbI_2$ with PbI_2 are formed, the lowest crystallising point being 344°. Experiments on the electrolysis of cuprous iodide were inconclusive, on account of the difficulty of preparing the compound in a satisfactorily pure condition. E. H. R.

Photochemical Cell with Complex Cyanides. S. Iimori (*J. Tokyo Chem. Soc.*, 1918, **39**, 1—13).—Platinum electrodes are immersed in solutions of complex cyanides (potassium nickel or potassium platinum), and one of the electrodes is exposed to light. This electrode becomes positive, whilst it became negative in the potassium ferrocyanide cells previously examined by the author. The current quickly decays when the circuit is closed through a high resistance. The author is of opinion that the *E.M.F.* pro-

duced with these complex cyanides is not of the same nature as that obtained in other solutions. CHEMICAL ABSTRACTS.

Electromotive Force of Alloys of Zinc and Cadmium with Tin, Lead, and Bismuth. PAUL FUCHS (*Zeitsch. anorg. Chem.*, 1919, **109**, 80—88).—The *E.M.F.* of elements composed of alloys of cadmium with tin, lead, and bismuth of various compositions as one electrode, cadmium sulphate solution and cadmium as the other electrode: alloy | N-$CdSO_4$ | Cd, have been measured; similar cells of the type: alloy | N-$ZnSO_4$ | Zn, in which zinc takes the place of cadmium in the alloy, have also been measured. The cells were measured in the presence of hydrogen, and only gave constant values after several days. The results confirm the views of Tammann (A., 1919, ii, 398) that the *E.M.F.* varies with the composition of the alloy only so long as one phase is present, that is, as long as the alloy is a solution or a single series of mixed crystals, but as soon as two phases appear, the *E.M.F.* is no longer dependent on the composition. J. F. S.

The Free Energy of Potassium Hydroxide in Aqueous Solution and the Activities of its Ions. MING CHOW (*J. Amer. Chem. Soc.*, 1920, **42**, 488—497).—Experiments were made to determine, by means of electromotive force measurements, the free energy attending the transfer of potassium hydroxide in aqueous solution from one concentration to another, and from the free energy decreases to derive the relative activities of the ions of the base and its activity coefficients at various concentrations (compare MacInnes and Parker, A., 1915, ii, 510, on the free energy of potassium chloride, and Ellis, A., 1916, ii, 369, and Noyes and Ellis, A., 1918, ii, 27, on hydrochloric acid). The cells studied were of the type $Hg+HgO-KOH(c_1)-K$ in $Hg-KOH(c_2)-Hg+HgO$ at 25°. The potassium amalgam was used in the form of a dropping electrode, and potassium hydroxide concentrations were varied between 0·003 and 0·84N. As found by Ellis in the case of hydrochloric acid, the activity coefficient at first decreases with increasing concentration. It passes through a minimum at about 0·5 molal concentration, then increases rapidly. Up to concentrations of 0·5 molal, the activity coefficient has a much smaller value than the conductance-viscosity ratio, showing that this ratio, even at moderate concentrations, is not even an approximate measure of the effective ionisation of highly ionised substances. E. H. R.

The Activities of the Ions in Solutions of Mixed Electrolytes. MING CHOW (*J. Amer. Chem. Soc.*, 1920, **42**, 497—502).—Determinations of the activity coefficients in mixed solutions of hydrochloric acid and potassium chloride were made from measurements of the electromotive force of cells of the type H_2(1 atm.) – $HCl(c_1)$ + $KCl(c_2)$ – Hg_2Cl_2 + Hg, in which the separate concentrations c_1 and c_2 were varied, but their sum was kept constant at 0·1N. The results show that the activity

coefficient of the hydrochloric acid has substantially the same valı in all the mixtures, and lend support to the view that the activit of the chlorine ion in solutions of different highly ionised un valent chlorides or of mixtures of them is determined by its ow concentration, and is independent of the cations associated wit it. The experimental results do not agree with those obtained t Loomis, Essex, and Meacham (A., 1917, ii, 353) from *E.M.l* measurements of the same type of cell. E. H. R.

The Theory of Electrolytic Ions. XIII. Conductivit of Multivalent Electrolytes. RICHARD LORENZ (*Zeitsch. anor Chem.*, 1919, **109**, 63—68. Compare A., 1919, ii, 262).—A corre tion and extension of the theoretical conceptions, on the step-wi ionisation and the degree of dissociation, put forward previous (*loc. cit.*). J. F. S.

The Phenomena of Electrolytic Migration. Electrolys of Mixed Solutions of Alkali Salts. MARC H. VAN LAI (*Rec. trav. chim.*, 1920, **39**, 301—329).—In the electrolysis of normal solution of sodium hydroxide at 18°, the yield from tl current is only 17·5% of that indicated by Faraday's law, but th yield is often varied by the superposition of different factors; thu according to the direction in which they act, the hydrostat pressure, diffusion, and electrical osmosis may favour the migr tion of certain ions and retard that of the ions of opposite sig Other intervening factors are temperature, the intensity of tl current, and the nature of the diaphragm between the anode ar cathode liquids. Thus, in the electrolysis of a solution of sodiu hydroxide, rise in temperature and cataphoresis both exert favourable influence. On the other hand, the diffusion of tl sodium hydroxide produces a loss, which increases with the co centration of the cathode liquid. As the concentration of tl current, I/V, diminishes, the yield first increases gradually unt it reaches a maximum and then decreases.

The electrolysis of a solution of sodium carbonate presents tl same fundamental characteristics as in the case of sodium hyd oxide, but in this case, as the electrolysis proceeds, the resistan of the cell increases, owing to the formation of sodium hydrog carbonate, the carbon dioxide liberated at the anode being entire absorbed by the solution at the ordinary temperature if tl current intensity is not too great. The introduction into the sol tion of an oxy-salt, such as the sulphate, chlorate, or nitrate sodium with a common cation, prevents the formation of sodiu hydrogen carbonate, and thus a cathode liquid very rich in sodiu hydroxide can be obtained. The nitrate gives the best result, ar the yield from the current increases with the concentration of tl oxy-salt.

Applying this method to barium carbonate in the presence barium nitrate, the solid carbonate being introduced into tl anode vessel, crystalline barium hydroxide was readily obtained W. G.

Diamagnetism of Odorous Substances. H. ZWAARDEMAKER and F. HOGEWIND (*Arch. Néerland. Physiol.*, 1920, **4**, 224—232).—The authors have measured the diamagnetism of a large number of odorous substances, and plotting the values found against the number of atoms in the molecule, it is found that, for an homologous series, the points lie on practically a straight line, but that the differences between the values obtained for adjacent members in a series vary from series to series. W. G.

A Method for Determining the Relationship between the Melting Point of a Crystal Lamella and its Thickness. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1920, **110**, 166—168).—The method suggested is to form by crystallisation a lamella of variable thickness between a plate and a cylindrical lens, and to have in the metal plate a temperature gradient so that the contact line between the plate and the lens is perpendicular to the isotherms in the plate. If the melting point lies between the temperatures of the two ends of the plate, part of the substance melts, and the bounding curve between the liquid and crystalline portions shows by its form the influence of the thickness of the lamella on the melting point. The work required to disrupt the crystal is inversely proportional to the thickness of the lamella, and it follows that the influence of the lamella thickness on the melting point is also inversely proportional to the lamella thickness. Thermodynamically, it is shown that the work required is equal to the change of equilibrium temperature multiplied by the entropy of unit mass at the melting point. E. H. R.

The Influence of State of Division on Melting Point. F. MEISSNER (*Zeitsch. anorg. Chem.*, 1920, **110**, 169—186).—The conclusions of Pavlov (A., 1909, ii, 19, 295, 800; 1910, i, 740) regarding the influence of size of particles on melting point are adversely criticised. The growth of large crystals at the expense of small ones is to be attributed, not to difference of vapour pressure between large and small crystals, but to fluctuations in temperature. Pavlov's observation that small particles of salol, 3 to 15 μ in diameter, melt several degrees below the normal melting point, could not be confirmed.

The only satisfactory method of examining the relation between state of division and melting point is by the investigation of thin lamellæ, formed by allowing a molten substance to crystallise between two plates. Such lamellæ admit of theoretical treatment, in which the surface energy of the crystal can be considered in the same manner as that of a liquid. If $A_0 - A'_0$ be the difference between the surface energies of crystal and liquid, the following relation holds: $A_0 - A'_0 = (T_1 - T_2)/T_0 \cdot RQ/2 \cdot d_1 d_2/(d_1 - d_2)$, where T_0 is the normal melting point, T_1 and T_2 the fusion temperatures of lamellæ of thickness d_1 and d_2 respectively, R the latent heat of fusion, and Q the density of the fused substance. To determine the value of $A_0 - A'_0$, it is necessary to know the relation between melting point and lamella thickness. The experimental method

used was that suggested by Tammann (preceding abstract), in which wedge-shaped lamellæ were formed between a cylindrical lens and a metal plate having a uniform temperature gradient from end to end. In the cases of azobenzene, tristearin, and myristic acid, the boundary curves formed between solid and liquid were distinctly displaced towards the cold end of the plate as the thickness of the lamella diminished. In the case of azobenzene, the displacement represented a difference of 0·355° in the melting point for a change of thickness from 0·8 to 10 μ. In the case of tristearin, the temperature difference was 0·199°, and for myristic acid 0·258°. The surface energy differences between crystal and liquid, calculated from the above equation, were in the three cases 67, 50, and 59 *ergs* respectively. In a number of other cases, including salol, acetamide, and glauber salt, the temperature difference was of the same order as in the case of myristic acid, whilst with *p*-chloroaniline and stearic acid, no difference due to diminishing thickness of the lamella could be detected.

E. H. R.

Phenomena Observed during the Melting, Freezing, and Boiling of Mixtures of Ammonium Chloride and other Chlorides. KURT HACHMEISTER (*Zeitsch. anorg. Chem.*, 1919, **109**, 145—186).—Cooling curves have been constructed for ammonium chloride, cuprous chloride, lithium chloride, zinc chloride, cadmium chloride, ferric chloride, thallous chloride, and lead chloride, and for mixtures of ammonium chloride with cuprous chloride, lithium chloride, zinc chloride, cadmium chloride, ferric chloride, thallous chloride, and lead chloride. Very complete diagrams of condition are constructed for the binary mixtures. In connexion with the simple salts, much of the data obtained differs from that previously published. The transition point of ammonium chloride is found to be 174° (Wegscheider, A., 1918, ii, 298, 184·5°). The following melting points are obtained: cuprous chloride, 425°; lithium chloride, 605°; zinc chloride, 283°; cadmium chloride, 568° (b. p. 964°); ferric chloride, 303°; thallous chloride, 427°; lead chloride, 501°. It is shown that by mixing other chlorides with ammonium chloride, this substance may be obtained molten. The compounds $CdCl_2,NH_4Cl$, $2ZnCl_2,NH_4Cl$, and $FeCl_3,NH_4Cl$, in addition to the double compounds already known, are indicated by the temperature composition diagrams. In the binary mixtures of ammonium chloride with cuprous chloride and lithium chloride, respectively, simple eutectics are formed, but no compounds. The compound formed between equimolecular quantities of ferric chloride and ammonium chloride is peculiar in possessing a definite boiling point, 386°. Mixtures of ammonium chloride with lead chloride and thallous chloride, respectively, cannot be melted. Ammonium chloride shows great similarity in its behaviour with other chlorides to the alkali chlorides. The nearer the two chlorides are in general properties, the simpler is the binary system formed between them.

J. F. S.

Melting Points of the Members of Homologous Series. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1919, **109**, 221—225).—A theoretical paper in which regular rise and fall of the melting point of members of the monocarboxylic aliphatic acids is discussed. It is suggested that the acids with an even number of carbon atoms exist in two stable, crystalline forms, and that this furnishes the reason for the course of the melting points in this series. In support of this hypothesis, it is shown that acetic acid exists in two such forms, the triple point of which lies at 57·5° under a pressure of 2330 kilos. per sq. cm. No such isomerides have been observed for the acid with an uneven number of carbon atoms, formic acid. J. F. S.

Critical Data and Chemical Constitution. W. HERZ (*Zeitsch. anorg. Chem.*, 1919, **109**, 293—296).—A theoretical paper in which the author has tabulated the critical pressure and critical temperature of a large number of members of the following homologous series: paraffins (9), olefines (3), methyl esters of the monocarboxylic aliphatic acids (6), ethyl esters of the same acids (6), ethers, amines (6), benzene hydrocarbons (11), aromatic amines (3), and other organic substances. It is shown that the critical temperature increases with increasing number of carbon atoms, and the critical pressure decreases with increasing number of carbon atoms. When the quotient of the critical temperature in absolute degrees and the critical pressure is divided by the number of carbon atoms, an approximate constant is obtained (2·5—4·0) for aliphatic compounds and 1·9—2·4 for aromatic compounds. A much better constant is obtained if, instead of the number of carbon atoms, the total number of atoms is used; here the constant is 0·99—0·69 for aliphatic compounds and 0·98—0·90 for aromatic compounds. Further, if the quotient is divided by the total number of valencies, a very good constant is obtained, 0·50—0·41 for aliphatic compounds and 0·43—0·37 for aromatic compounds. J. F. S.

New Instrument for Measuring Vapour Tension. HAROLD MOORE (*J. Soc. Chem. Ind.*, 1920, **39**, 78—80T).—An instrument for making rapid and accurate measurements of the vapour pressure of motor spirit is described. It consists of two tubes about $\frac{1}{4}$ in. bore and 800 mm. long connected to each other and to a levelling bottle by means of a Y-piece and thick-walled rubber tubing. The two tubes are clamped vertically, and have mercury-sealed cocks at their upper ends, which close the tubes to small, graduated cups. One of the tubes is surrounded by a water-jacket. To make a measurement, the whole apparatus is filled with mercury, then a measured volume of spirit is admitted into one of the tubes from the small cup at the top, and the reservoir lowered. The barometric height is read from one tube, and the barometric pressure diminished by the vapour pressure of the spirit is read from the other tube. The vapour pressure of crystallisable benzene, ethyl alcohol, and petrol has been deter-

mined over the temperature range 10—50°, and also the vapou pressure of a series of mixtures of alcohol and petrol and alcoho and benzene at 20°, 30°, 40°, and 50°. Working with water, th error observed in the vapour pressure was about 3 mm., but witl mixed motor spirits it will probably be much greater. J. F. S.

The Vapour Pressures of Cadmium, Lead, and Ti Amalgams. JOEL H. HILDEBRAND, A. H. FOSTER, and C. W BEEBE (*J. Amer. Chem. Soc.*, 1920, **42**, 545—548).—A continu ation of previous work on the vapour pressures of liquid amalgam (compare A., 1913, ii, 471, 755; 1914, ii, 800; 1916, ii, 14). Th vapour pressures of mercury over amalgams of cadmium, lead, an tin were measured at 324°, by the method previously described at intervals covering the entire range of concentrations, and th values of the constants *a* and *c* were calculated in the empirica equation $\log p/p_0 = \log N + a/(1+cn)^2$, where n represents th number of molecules of mercury per molecule of the other metal $N = n/n+1$, p_0 is the vapour pressure of pure mercury, and p tha of the amalgam of composition corresponding with n. Cadmiun amalgams show vapour pressures less than those demanded b Raoult's law, $p/p_0 = N$, and the deviations can be calculated on th assumption of partial solvation, varying with the concentratio according to the mass law, to form molecules of CdHg. Lea and tin amalgams give practically equal vapour pressures, whic are much greater than Raoult's law demands. The deviation cannot be accounted for by the assumption of any simple molecula change. E. H. R.

The Aqueous Pressure of some Hydrated Crystals Oxalic Acid, Strontium Chloride, and Sodium Sulphate GREGORY PAUL BAXTER and JOHN ERNEST LANSING (*J. Amer Chem. Soc.*, 1920, **42**, 419—426).—With the object of perfecting a trustworthy method of measuring the aqueous pressures o hydrated crystals, experiments were made with oxalic acid strontium chloride, and sodium sulphate, and the following metho was found to give satisfactory results. The hydrated crystal were intimately mixed with 5—10% by weight of the dehydrate substance, and the mixture was packed, interspersed with glas beads, in a large U-tube. The method of experiment was to pas a measured volume of dry air through the column of crystals a constant temperature, subsequently passing the air throug weighed drying tubes containing phosphoric oxide. The curve obtained by plotting the logarithm of the vapour pressure foun against the reciprocal of the absolute temperature were very nearl straight lines, almost exactly so in the case of sodium sulphat crystals. E. H. R.

The Vapour Pressures of Concentrated Solutions. G. R PARANJPÉ (*J. Ind. Inst. Sci.*, 1918, **2**, 59—72).—Measurement were made between 0° and 40° of the vapour pressures of solu-

tions of (1) potassium hydroxide for concentrations between 18·81 and 138·2 grams of the anhydrous hydroxide in 100 grams of water; (2) sodium hydroxide for concentrations between 14·62 and 113·1 grams in 100 grams of water; (3) calcium chloride for concentrations between 14·81 and 119·5 grams of the anhydrous salt in 100 grams of water. The results obtained for potassium hydroxide are not in very close agreement with those obtained by Dieterici (compare A., 1891, 783; 1898, ii, 207; 1899, ii, 403).
W. G.

Determination of Boiling Point. SCHIMMEL & Co. (*Bericht.* April-October, 1919, 100—102; from *Chem. Zentr.*, 1920, ii, 422—423).—In connexion with the apparatus described recently by Paul and Schautz (A., 1919, ii, 422), the authors recommend the adoption of definite normal pressures for data concerning boiling points, particularly for such as are determined in a vacuum. As absolute unit of pressure, the bar (one dyne per sq. cm.) is advocated. One atmosphere = 1,013,200 bars, or 10 kilobars correspond fairly closely with 75 mm. Measurements should be effected at normal pressures, a simple type of apparatus for the measurement of the latter being depicted in the original. Measurement of pressure in vacuum distillation (particularly in a high vacuum) is only accurate when it is effected close to the point at which the temperature is observed. The errors in the older method, in which the manometer is attached to the exhaust pipe, increase with increase of the vacuum and the velocity of distillation, with the decreasing width of distillation and condensing tubes, and with leaks in the apparatus. H. W.

Physical Behaviour of Liquids. W. HERZ (*Zeitsch. Elektrochem.*, 1920, **26**, 109—111).—A theoretical paper in which formulæ are developed whereby the molecular boiling-point elevation and the capillarity constant at the boiling point may be calculated from the critical data. These formulæ have the form: (1) $c = 4T_k^2 d_k/3p_k$; (2) $a = 0{\cdot}03643 p_k/d_k$, in which p_k is the critical pressure, T_k the critical temperature, d_k the critical density, c is the molecular elevation constant, and a the Poisson capillarity constant. A further formula for calculating the vapour pressure is also developed; this has the form

$$\log(p_s/p_1) = 4{\cdot}91(T_s/T_1 - 1),$$

in which p_s is the vapour pressure at the boiling point T_s, and p_1 the vapour pressure at the temperature T_1. The values obtained by the use of these formulæ have been compared with the experimental values, and found in the case of non-associated liquids, both organic and inorganic, to be in good agreement. J. F. S.

Vapour Tension and Heat of Vaporisation, and the Dependence of the Factors *a* and *b* on the Temperature and the Volume. J. J. VAN LAAR (*Rec. trav. chim.*, 1920, **39**, 215—242).—A mathematical discussion of the subject. W. G.

A Thermodynamic Investigation of Reactions Involving Silver Sulphide and Silver Iodide. ARTHUR A. NOYES and E. STANLEY FREED (*J. Amer. Chem. Soc.*, 1920, **42**, 476—487).—The equilibrium at 25° of the reaction

$Ag_2S(solid) + 2H^+I^-(in\ water) = 2AgI(solid) + H_2S(in\ water)$

was studied with the object of determining how the activity coefficient (or effective ionisation) of the acid varies with its concentration, and to determine the free energy change attending the reaction. The concentration of hydriodic acid was necessarily confined within the limits 0·024 to 0·116*N*. The equilibrium constant, *K*, calculated from the formula $K = C_{H_2S}/(C_{HI}\gamma)^4$, where γ is the ionisation constant, has a mean value 964. Assuming that the activity coefficient at $C_{HI} = 0·025N$ is identical with the ionisation constant, it is found that between concentrations 0·025 and 0·12 the activity coefficient decreases 4·5%, compared with 8·3% found by Noyes and Ellis for hydrochloric acid (A., 1918, ii, 27).

E.M.F. measurements were made between 5° and 25° of the cells

$H_2(1\ atm.) - HCl(0·5—0·1N) -$
$\{HCl(0·5—0·1N), H_2S(1\ atm.)\} - Ag_2S + Ag,$

and at 25° of the cells

$H_2(1\ atm.) - HI(0·30—0·98N) - AgI + Ag.$

From the data obtained, a number of free energy calculations are made, and are compared with the results of calculations made using data from other sources. Finally, the following figures are adopted: for the free-energy decrease attending the reaction $2AgI + H_2(1\ atm.) = 2Ag + 2H^+ + 2I^-$ at 25°, −6885 cal., and for the reaction $Ag_2S + H_2(1\ atm.) = 2Ag + H_2S(1\ atm.)$ at 25°, −1485 cal. Making use of the value found for the free energy of formation of iodide ion by Lewis and Randall (A., 1914, ii, 840) the free-energy valne for the reaction $2Ag + I_2 = 2AgI$ is found to be +31,493 cal. Half this quantity is the free-energy decrease attending the formation of one molecule of solid silver iodide from its elements at 25°. E. H. R.

Use of Lead Electrodes for Thermochemical Measurements. CONSTANZE KRAHMER (*Zeitsch. Elektrochem.*, 1920, **26**, 97—104).—The *E.M.F.* of cells of the type

$Pb | PbCl_2(sat.) || Hg_2Cl_2 | Hg,$

$Pb | PbCl_2(sat.) || AgCl | Ag$, $Pb | PbBr_2(sat.) || AgBr | Ag$, and

$Pb | PbI_2(sat.) || AgI | Ag$

has been measured at a number of temperatures, and from the data thus obtained the heat of formation of lead chloride, silver bromide, and silver iodide has been calculated. The lead electrodes were prepared on platinum wire by electrolysing a solution of 8% hydrofluosilic acid and 4% lead silicofluoride by means of a current of 0·001 ampere. The *E.M.F.* of the cell

$Pb | PbCl_2(sat.) || Hg_2Cl_2 | Hg$

is given by the formula $E_{293} = 0·53113 - 0·000191(20 - t)$, and the

heat of the reaction $\frac{1}{2}Pb+HgCl=\frac{1}{2}PbCl_2+Hg$ is $U_{293}=10,949\pm 0.1\%$ cal., from which the heat of formation of lead chloride is calculated to 85,521 cal. In the case of the cell

$$Pb \mid PbCl_2(sat.) \parallel AgCl \mid Ag,$$

$E_{293}=0.49328+0.000125(t-20)$, $U_{293}=12,211\pm 24$ cal., and assuming the heat of formation of silver chloride to be 30,505 cal., the heat of formation of lead chloride is 85,432 cal. The *E.M.F.* of the cell $Pb \mid PbBr_2(sat.) \parallel AgBr \mid Ag$ is

$$E_{293}=0.35252+0.000126(20-t^{\circ})$$

and $U_{293}=8974\pm 44$ cal.; using the value 66,350 cal. for the heat of formation of lead bromide, the heat of formation of silver bromide is found to be 24,201 cal. In the case of the cell

$$Pb \mid PbI_2(sat.) \parallel AgI \mid Ag,$$

$E_{293}=0.21205+0.000129(20-t)$ and $U_{293}=5758\pm 57$ cal., and the heat of formation of silver iodide is 15,192 cal. When the haloids used were crystalline, slightly different values are found for the above-named cells. A number of experiments with evacuated elements show that the gradual falling of the *E.M.F.* of the cell $Pb \mid PbCl_2(sat.) \parallel Hg_2Cl_2 \mid Hg$ is not due to oxidation, but is in some way connected with the size of the lead crystals. A table of comparison of the present values with those of Thomsen, Berthelot, and other observers is included in the paper. J. F. S.

Heat of Solution. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1920, **109**, 215—220).—A theoretical paper in which it is shown that from a knowledge of the heat of solution of one substance in another, it is possible to decide whether or no a chemical reaction has taken place during solution. The heat of solution is made up of heat quantities brought about by (i) the conversion of an anisotropic substance into an isotropic condition, (ii) the mixture of the isotropic substance with the solvent, and (iii) chemical processes, such as formation of compounds, change in molecular weight, and ionisations. The dimensions of the first two quantities can be calculated theoretically, hence from the experimentally determined heat of solution it is possible to see whether any heat change due to the third cause is contained in the experimental value, and so ascertain whether chemical processes have taken place. J. F. S.

Heat of Solution and the Partial Molal Heat Content of the Constituents in Aqueous Solutions of Sodium Chloride. MERLE RANDALL and CHARLES S. BISSON (*J. Amer. Chem. Soc.*, 1920, **42**, 347—367).—The partial molal heat content of a substance is its heat content when in solution at a given concentration, and is defined as the increase in the heat content of a large amount of the solution at the given concentration when one mol. of the substance is added to it. The symbol $\bar{H}$ is used for this quantity, and H for the absolute molal heat content of the substance. It follows that the partial molal heat of solution of a substance, for example, sodium chloride, is given by $\bar{H}_c - H_{NaCl}$

for a concentration c. The symbol ΔH is used to represent the partial molal heat content of a substance formed from its elements in their standard state at the same temperature. The specific heats of sodium chloride and potassium chloride solutions were first determined for different concentrations at 25°. The partial molal heat of solution of water in sodium chloride solution, $\bar{H}-H_{H_2O}$, was determined by measuring the heat absorbed per mol. of water when water was added to sodium chloride solutions of known concentrations. Starting with saturated sodium chloride solutions, the values rise gradually from about 11 cal. at 6·25*M* to 21 cal. at 4·2*M*, and then gradually diminish to zero at infinite dilution.

The heat of dilution of sodium chloride was also measured calorimetrically by adding small amounts of saturated solution to a large volume of water. The value found at infinite dilution was 606 cal. The mean heat of solution of sodium chloride in a very large amount of water was found experimentally to be 1019 cal. From the values obtained, the partial molal heat content of sodium chloride, ΔH, at 25° in solution at all concentrations was calculated. The value of ΔH increases from −96,781 at infinite dilution to −97,500 in a saturated solution, whilst the partial molal heat content of the water decreases from −68,272 at infinite dilution to −68,250 at 4·2*M*, increasing again to −68,261 in a saturated solution. E. H. R.

Chemical Affinity. XII. Thermodynamical Relationship between the Mixture Affinities of Partially Saturated Solutions and its Application to the Estimation of Affinity. J. N. Brönsted (*K. Danske. Vidensk. Medd. Math. Phys.*, 1918, **1**, No. 5, 1—39; from *Chem. Zentr.*, 1920, i, 404—405. Compare this vol., ii, 298).—A relationship has been established between the mixture potentials of two components in a mixture in which the potential of the other substances present is maintained constant, as, for example, by invariably using solutions saturated with these substances. The relationship may be expressed by the equation $x.dA_1/dx+(1-x)dA_2/dx=0$ or $n_1dA_1+n_2dA_2=0$, in which A_1 and A_2 are the molecular differential mixture potentials of the components, and n_1 and n_2 the number of molecules in the mixture. The equation has therefore the same form as if the two components are present in binary mixtures. The theory is developed for the formation of double salts, for allotropic transformation, and for reciprocal pairs of salts, and is applied in particular to the cases of α- and β-$CaCl_2,4H_2O$ and of carnallite and schönite. The affinity of the reactions $KCl+NaClO_3 \longrightarrow KClO_3+NaCl$ and $KCl+NaNO_3 \longrightarrow KNO_3+NaCl$ has been measured at 16·39° by estimation of the vapour pressure; the values 2020 cal. and 740 cal. are obtained, which agree closely with the data previously deduced from electrometric measurements, and thus afford a sharp verification of the theory. An experimental method is also described which permits the simultaneous estimation of

vapour tension and concentration of solutions, and also indicates in a simple manner the points at which saturation in respect to one or two components occurs. H. W.

A Surface Tensimeter for Small Quantities of Liquids. C. C. KIPLINGER (*J. Amer. Chem. Soc.*, 1920, **42**, 472—476).—A method has been devised by means of which the surface tension of a liquid may be determined when only a drop or two is available. A capillary glass tube, about 18 cm. long, 1 mm. internal and 4 mm. external diameter, is carefully made with its ends, as nearly as possible, plane and accurately rectangular with the length. By means of a special device (A., 1918, ii, 360), the tube can be attached to a quadrant cut from a celluloid protractor. A small notch cut in the apex of the quadrant holds in position a thread, which passes over it, the thread carrying a small weight at each end and serving to indicate the angular displacement of the tube. The apparatus is held in position by a suitable clamp on a stand. A short column of the liquid to be examined is introduced into the clean, dry capillary tube, and the tube is turned through such an angle that the meniscus at the lower end changes to a plane surface. The point at which this occurs is observed by means of a pocket lens, and the angular displacement from the vertical is read off on the quadrant. The length, l, of the column is measured to 0·1 mm., and from the equation $l \cos A = h$, the height, h, of the vertical column exerting the same pressure as the inclined column of liquid is calculated. The surface tension is then calculated from the usual formula, $T = d \times h \times r \times 980/2$ dynes per cm. The results obtained are generally 2—4% low. The method may be used to assist in identifying organic liquids. E. H. R.

Adsorptive Power of Different Forms of Charcoal. K. SCHERINGA (*Pharm. Weekblad*, 1920, **57**, 348—350).—The most adsorptive charcoal was obtained by heating the material to be charred to a high temperature. Low-temperature carbonisation of filter paper, or previons impregnation of the material with sodium chloride, gave an inferior adsorbent. W. S. M.

Some Aspects of the Behaviour of Charcoal with respect to Chlorine. G. S. BOHART and E. Q. ADAMS (*J. Amer. Chem. Soc.*, 1920, **42**, 523—544).—Experiments on the absorption of chlorine by charcoal showed considerable variations in the behaviour of single samples, which could only be attributed to differences in the humidity of the current of chlorine-laden gas. A series of experiments was therefore carried out on the effect of moisture and, in addition, the influence of variations in temperature and pressure, of the velocity of the gas through the charcoal and of the density of the charcoal and the depth of the absorbing layer, were studied. Two processes take place during the passage of the gas through the charcoal, absorption or adsorption, which cannot be distinguished, and catalytic formation of hydrochloric acid. The results of the

experiments are illustrated by means of curves, in which the percentage of chlorine or hydrochloric acid transmitted is plotted against time. The period during which no chlorine or hydrochloric acid is transmitted is called the service time of the charcoal. The service times of different charcoals could not be correlated with their apparent density. For any one sample of charcoal, the service time increases more rapidly than the thickness of the absorbing layer. Charcoals with the greatest chlorine capacity were found to be the best catalysts for the reaction between water and chlorine. The effect of humidity was studied by varying the moisture content of the gas stream, air to chlorine in the ratio 500 : 1, from 0—80% saturation at 25°. Hydrogen chloride always appeared in the transmitted gases before chlorine, and when chlorine appeared as well, the effect of the moisture could be seen, particularly in the 80% saturation experiment, in the greater proportion of acid to free chlorine. The duration of complete chlorine absorption passes through a minimum at about 50% saturation. Below 12·5°, chlorine appeared in the gases before hydrogen chloride; above this temperature, the reverse was the case. The service time is at a minimum between 0° and 12·5°. Reductions in pressure have little, if any, effect. The chlorine capacity of the charcoal is increased by one exposure to chlorine, followed by heating to dull redness in a vacuum. E. H. R.

The Velocity of Adsorption of Chloropicrin and Carbon Tetrachloride by Charcoal. HERBERT S. HARNED (*J. Amer. Chem. Soc.*, 1920, **42**, 372—391).—The experiments recorded were carried out for the purpose, first, of obtaining reproducible results in the measurements of the velocity of adsorption of gases on a relatively gas-free solid surface, and, secondly, of determining the effect of a foreign gas on this velocity. The method of experiment adopted was to expose the charcoal for a measured time to the vapour to be adsorbed at a low pressure (the vapour pressure of the compound), and to determine the amount of adsorption by the increase in weight of the charcoal. Charcoal was chosen for examination on account of its exceedingly large adsorbing surface, and chloropicrin and carbon tetrachloride as gases on account of their relatively high molecular weight, and the consequently relatively considerable weight of gas adsorbed. The results are shown by series of curves, in which the weight of gas adsorbed per gram of charcoal is plotted against time. In no case could reproducible results be obtained until the charcoal had been heated to more than 700° in a vacuum, cooled in a vacuum, exposed to the gas until a considerable quantity was adsorbed, and again heated above 700° in a high vacuum. This process of washing out with the gas under examination is necessary to remove foreign gases, which cause an initial lag in the adsorption. When the charcoal is in such a condition that the maximum velocity of adsorption is attained, the process follows the equation

$$m = 1/t \, . \log A/A - K,$$

where K is the amount adsorbed per gram of charcoal in time t and A is the amount adsorbed when t is infinite, m being a constant. The curve obtained by plotting $\log A/A-K$ against t is then a straight line. The results are in agreement with Langmuir's theory of adsorption (A., 1918, ii, 430), in which he assumes that the adsorbed layer of gas is only one molecule deep. Some of the results for carbon tetrachloride indicate the possibility of the formation to a certain extent of a second adsorbed layer, but the influence of small quantities of foreign gases on the rate of adsorption may account for the divergence of the curves, in these cases, from straight lines. E. H. R.

Evaluation of Dissociation Measurements of [Metal] Ammines by means of the Nernst Theorem and Nomograms. WILHELM BILTZ and GUSTAV F. HÜTTIG (*Zeitsch. anorg. Chem.*, 1919, **109**, 111—125. Compare this vol., ii, 318).—A theoretical paper in which the method of evaluating and comparing dissociation pressures of ammines is described. The heat of dissociation at the absolute zero (Q_0) and the coefficient of T are determined from the Nernst equation $\log p = -Q_0/4{\cdot}57T + 1{\cdot}75 \log T + (\Sigma\nu\beta + \Sigma nb)/4{\cdot}57 \,.\, T + 3{\cdot}3$. Nomograms are given by means of which the calculations, both for the complete and the approximate Nernst formula, are replaced by readings from scales. The value of Q_0 is shown to be constant in the case of the ammines of iron, cobalt, nickel, and manganese, and is in agreement with the calorimetric values and those calculated according to the van't Hoff rule. The coefficient of T is, within the limits of experimental error, in keeping with the thermochemical data; it is independent of the nature of the ammonia-free salt, but depends on the nature of the linking of the combined ammonia. The combined ammonia has a larger molecular heat in the hexammines than in those compounds with less ammonia. The dissociation temperature of all the ammines is determined by the nomograph for $p=100$ mm. The values are compared with those obtained by a graphic approximation method, and the two sets of values shown to be in moderate agreement. The nomographic method is superior to the graphic method, and also more convenient in use. J. F. S.

Nomographs from the Functions Log $p = -Q/4{\cdot}57T + 1{\cdot}75$ Log $T + C$ and Log $p = -Q/4{\cdot}57T + 1{\cdot}75$ Log $T - aT + 3{\cdot}3$. H. VON SANDEN (*Zeitsch. anorg. Chem.*, 1919, **109**, 126—131. Compare preceding abstract).—A theoretical paper in which the method of drawing and using nomographs is described. A nomograph is a series of lines and curves by which the relationships of functions with several variables may be represented (see "Traite de Nomographie," d'Ocagne). In the case of the two functions named above, the nomograph is constructed as follows. Two vertical lines are drawn, of which the one standing to the left is graduated for pressure in millimetres of mercury; the other is divided to

give values of Q; to the right of these lines, a series of curves are drawn, one for each value of C or a, and each of these curves is subdivided to give temperature values. To illustrate the use of the nomograph thus constructed, an example will best serve. Suppose Q, T, and C are known and the corresponding value of p is desired. The value of T on the appropriate C curve is sought out, and the point joined by a straight line with the corresponding Q value. The line is then produced, and the point where it cuts the pressure line gives the corresponding p value. J. F. S.

Diffusion of Organic Substances in Organic Solvents and the Examination of Stokes' Formula. ERNST DUMMER (*Zeitsch. anorg. Chem.*, 1920, **109**, 31—51).—The author has determined the diffusion coefficient, the viscosity, and index of refraction of nitromethane, ethyl acetate, nitrobenzene, benzotrichloride, acetone, ethyl benzoate, and methyl alcohol, and solutions of these substances in one another. From the results, the radius of the various molecules is calculated by means of the Stokes-Einstein formula $D=RT/N.1/6\pi rk$, in which $R=8\cdot32\times10^7$ and $N=6\cdot20\times10^{23}$, and these values are compared with the theoretical values. It is shown that the radius in a given case is different depending on the molecular weight of the diffusing substance anc the solvent. Certain regularities are apparent in the results thus a smaller value is found for the radius of a given substanc the larger the molecular weight of the solvent. An exception t this is found only in the calculation of the radius from th diffusion of ethyl benzoate into methyl alcohol, and from th diffusion of nitrobenzene into methyl alcohol. From the results, i can be stated generally that the Stokes-Einstein formula may onl be applied to the region of molecular dimensions with the greate caution. J. F. S.

Solubility. I. Solubility of Salts in Solutions of Salt J. N. BRÖNSTED (*K. Danske. Vidensk. Medd. Math. Phys.*, 191 **2**, No. 10, 1—46; from *Chem. Zentr.*, 1920, i, 402—403).—T theory of the solubility of salts in solutions of salts is develop on the preliminary hypothesis that the coefficient of activity a mixed salt solution is the same for every ion of the same ty The calculation of the coefficient of activity, f, is based on observation of Noyes and Falk that the behaviour of a num of binary salts can be summarised by the expression $2-i=K$ in which i is van't Hoff's factor, c the equivalent concentrati and K a constant which is characteristic for each salt; by substitution of $2a=K$, the following equation is deriv $\log^{10}f=-1\cdot373a\sqrt[3]{c}=-a\sqrt[3]{c}$. The development of the th depends on whether the solvent and dissolved substance hav common ion or not; both cases are considered and illustrated experimental data. The following solubilities are cited: dichl tetramminecobalt thiocyanate in sodium chlorate solution; t dinitrotetramminecobalt in potassium formate solution; c

tetramminecobalt perchlorate in sodium formate solution; dichlorotetramminecobalt bromide in potassium bromide solution; *trans*-dinitrotetramminecobalt chloride in potassium chloride solution; *iso*thiocyanopentamminecobalt sulphate in magnesium sulphate solution. H. W.

Supersaturation and Crystal Size. WILDER D. BANCROFT (*J. Physical Chem.*, 1920, **24**, 100—107).—A theoretical paper in which the theory put forward by von Weimarn in connexion with the relationship between the degree of supersaturation and the size of crystals ("Grundzüge der Dispersoidchemie," 1911, 39) is discussed and shown to be inadequate, because it does not take account of the number of nuclei formed. It is shown that, with vigorous stirring and increasing supersaturation, a substance, which normally is precipitated anhydrous, may be obtained as a colloidal solution, a curdy precipitate, fine crystals, coarse crystals, or a gelatinous precipitate. At higher temperatures, precipitates are, as a rule, more coarsely crystalline than at lower temperatures. The theory of von Weimarn applies to solutions which are not stirred. The conditions for forming large crystals are those in which there is no spontaneous formation of nuclei and in which the rate of crystallisation is so slow that branched crystals do not form. The effect of adsorption on the growth of crystals is not adequately covered by von Weimarn's theory. J. F. S.

The Relation between Growth Forms and the Structure of Crystals. PAUL NIGGLI (*Zeitsch. anorg. Chem.*, 1920, **110**, 55—80).—A theoretical paper in which the modern theory of crystal structure is applied to the discussion of the development of crystal forms both during the growth of a crystal and during its dissolution. The faces which attain maximum development are perpendicular to the directions of maximum velocity of growth, and these faces correspond with the principal planes in the lattice structure. The whole crystal is regarded as a polymerised co-ordinated compound; the inner atoms are saturated, but those on the surface are unsaturated in certain directions. It is shown that, since the directions in which the unsaturated valencies are active are determined by the structure of the crystal, faces with complex indices should grow with greater velocity than simpler faces, because the development of such complex faces exposes to a greater extent the free atomic valencies. To a certain depth, which can be calculated, the crystal can be regarded as imperfectly formed in the plane of these complex faces, and the greater the depth of this partly crystalline layer, the greater will be the velocity of growth of the corresponding face. Statistical calculations for different types of cubic crystals show that the theoretically most probable faces are those which indeed actually occur, for example, in crystals of sodium chloride and zinc blende. The occurrence of vicinal faces is also in accordance with the theory. E. H. R.

Structure Distortion in Plastic Fluid Crystals. O. Lehmann (*Ann. Physik*, 1920, [iv], **61**, 501—532).—An account of some experiments on the optical properties of fluid crystals. Mixed fluid crystals, for example, cholesteryl chloride and propionate, when mechanically distorted between a microscope slide and cover slip, exhibit optical rotation, varying in magnitude and direction with the proportions of the two constituents present. E. H. R.

Electrical Double Refraction of Colloids. C. Bergholm and Y. Björnståhl (*Physikal. Zeitsch.*, 1920, **21**, 137—141).—Sols of vanadium pentoxide, gold, and silver have been examined, by means of a method employed by Brace (*Phil. Mag.*, 1904, [vi], **7**, 317), under the influence of an alternating electric field, and in every case shown to be double refracting. This implies that the particles of these sols are not spherical and do not possess spherical symmetry. The double refraction in a gold sol, the particles of which have a diameter of about 100 $\mu\mu$, changes with the frequency; with a potential of 400 volts per cm., the phase difference is 35% greater at 3000 periods than at 50 periods. J. F. S.

The Gold Numbers of Protalbic and Lysalbic Acids. Ross Aiken Gortner (*J. Amer. Chem. Soc.*, 1920, **42**, 595—597).—The gold numbers of protalbic and lysalbic acids, determined by Zsigmondy's process (A., 1903, i, 135), are 0·15—0·20 and 0·10—0·125 respectively. Comparison of these with those for dextrin (125—150), soluble starch (10—15), sodium oleate (2—4), egg-albumin (0·08—0·10), and gum arabic (0·10—0·125) suggests that the protective action of the acids in question has been much overrated. J. K.

The Coagulation of Clay Suspensions and Silicic Acid. Otto M. Smith (*J. Amer. Chem. Soc.*, 1920, **42**, 460—472).—The experiments recorded were made with the object of determining the action of electrolytes commonly occurring in natural waters on the stability of colloidal clay suspensions and silicic acid held in solution, and their effect when aluminium sulphate is used as a coagulant. Experiments on the precipitation of silicic acid by alkalis in the presence of aluminium salts showed that the optimum hydrogen-ion concentration for the precipitation of the aluminium hydroxide and the removal of the silicic acid is 1×10^{-8}. The limiting values of the hydrogen-ion concentration between which the solid aluminium hydroxide phase is present are 1×10^{-4} and 1×10^{-11}. If the alkali (sodium hydroxide) is added all at once, the presence of silicic acid prevents the precipitation of aluminium hydroxide, apparently by acting as a protective colloid. The presence of bivalent cations, however, destroys this protective power. The effect of a number of electrolytes on the coagulation of clay suspensions by aluminium sulphate was studied. The electrolytes examined, arranged in their order of efficiency as coagulants, were: aluminium sulphate, calcium and barium hydr-

oxides, *calcium chloride, magnesium* sulphate, magnesium and calcium *hydrogen carbonates*. The ratio of efficiency of aluminium to calcium and barium ions is about 5 to 1. Sodium hydroxide, hydrogen carbonate, carbonate, and sulphate have a singular influence on the coagulating effect of aluminium sulphate. With a given amount of sodium hydroxide, for example, and gradual addition of aluminium sulphate to the clay suspension, there is first increased dispersion, then coagulation, followed by renewed dispersion and a second coagulation. The second disperse phase is not as stable as the first. The presence of silicic acid has in all cases a retarding effect on the coagulation by aluminium sulphate, whatever salts may be present. E. H. R.

Emulsions. III. T. R. BRIGGS [with J. C. ASHMEAD, C. F. TEARS, and L. H. CLARK] (*J. Physical Chem.*, 1920, **24**, 120—126. Compare A., 1915, ii, 531).—The time required to emulsify a series of mixtures of benzene and 1% solutions of sodium oleate has been determined for various methods of mixing. Mechanical shaking, intermittent hand shaking, with measured interval between the shakes, continuous hand shaking, and rolling the bottles containing the mixtures were compared. It is shown that intermittent shaking is far more efficient than uninterrupted shaking, even in a shaking machine. The time and number of shakes required to complete an emulsification both vary with the rest interval between the shakes. Emulsions are easily made by rolling or rotating cylindrical bottles containing oil and soap solution. This method of procedure is similar to the "Continental" method (see following abstract). The ideal emulsifying process is one causing the benzene to break up into drops with the least disintegration of the aqueous soap solution. J. F. S.

Emulsions. IV. T. R. BRIGGS, F. R. DU CASSÉ and L. R. CLARK (*J. Physical Chem.*, 1920, **24**, 147—160).—The preparation of emulsions by the continental method is investigated in the case of olive oil. The method consists in preparing an emulsion nucleus by grinding together in a mortar definite quantities of oil, water, and gum, and then diluting with the requisite quantity of water. It is shown that the hypothesis of Roon and Oesper (A., 1917, ii, 299) that hydration of an emulsifying colloid must take place at the moment of disintegrating the oil is not in accordance with experiment. Even in a mortar, emulsions may be made with previously hydrated colloids. Emulsions are easily produced by the method of trituration in a mortar if the area of the interface between oil and water is made sufficiently large. One method by which this may be achieved is to suspend finely divided solids, which are easily wetted, in the oil. The effectiveness of the solid is increased by decreasing the average size of the particles. Up to a certain limit, the readiness with which an emulsion forms increases as the quantity of solid added. It is preferable to suspend the solid in the liquid before adding the

dispersing solution. The most effective solids are those readily wetted by the dispersion medium. In the continental method, gum arabic (acacia) plays the part of finely divided solid and emulsifying colloid. The finely divided solid serves to increase the interface between oil and water. Wetting phenomena may also cause the displacement of one liquid by the other, and consequently give rise to disintegration of the displaced liquid. Emulsions of water in oil may be made in a mortar in the presence of finely divided solids easily wetted by oil. J. F. S.

Physical Chemistry of Rusting. II. Equilibria in the System Lead–Sulphur–Oxygen. W. REINDERS (*Zeitsch. anorg. Chem.*, 1919, **109**, 52—62. Compare A., 1915, ii, 47, 773).—A criticism of a paper by Schenck and Albers (A., 1919, ii, 222) on *the equilibria in the system lead–sulphur–oxygen, in which it is* shown that the experimental results are not trustworthy and will not bear the interpretation put on them. Of the five quintuple points characterised, two are shown to be impossible, and five other equilibrium curves are also not in keeping with known facts.

J. F. S.

Chemical Affinity. XI. The Transformation of Reciprocal Pairs of Salts and the Equilibrium of Benzidine and Benzidine Sulphate. J. N. BRÖNSTED and AGNES PETERSEN (*K. Danske. Vidensk. Medd. Math. Phys.*, 1917, 1, No. 3, 1—21; from *Chem. Zentr.*, 1920, i, 425—426. Compare A., 1915, ii, 221).—The affinity of the reaction $KCl + NaBr \longrightarrow KBr + NaCl$ has been estimated to be 1620 cal. by an electrochemical method, using hydrogen, tartaric acid, and alkali tartrates; the following elements were measured: (1) $H_2 | H_2C_4H_4O_6,KHC_4H_4O_6,KCl | HgCl,Hg$; (2) $H | H_2C_2H_4O_6,NaHC_4H_4O_6,H_2O,NaCl | HgCl,Hg$; (3) $H | H_2C_4H_4O_6,KHC_4H_4O_6,KBr | HgBr,Hg$;

(4) $H | H_2C_4H_4O_6,NaHC_4H_4O_6,H_2O,NaBr,2H_2O | HgBr,Hg$.

The affinity of the transformation $KCl + \frac{1}{2}Na_2SO_4 \longrightarrow \frac{1}{2}K_2SO_4 + NaCl$ was measured in the following manner. As a consequence of the formation of glaserite, the system of the three salts is unstable, but the two systems $KCl + K_2SO_4$ and $NaCl + Na_2SO_4$ are separately completely stable. If sulphuric acid of the same potential is added to each system, the following actions occur: $\frac{1}{2}H_2SO_4 + KCl = \frac{1}{2}K_2SO_4 + HCl$ and $\frac{1}{2}H_2SO_4 + NaCl = \frac{1}{2}Na_2SO_4 + HCl$; hydrochloric acid is thus liberated at two potentials, the *difference of which is a measure of the affinity of the change.* The two potentials were measured by hydrogen and calomel electrodes. The authors endeavoured to secure equality in the sulphuric acid potential in the two systems by the addition of a mixture of benzidine and benzidine sulphate, or of the latter alone; it was expected that elimination of sulphuric acid would occur in accordance with the scheme $C_{12}H_8(NH_2)_2,H_2SO_4 \longrightarrow C_{12}H_8(NH_2)_2 + H_2SO_4$ until the solution had attained a sulphuric acid potential independent of the other components. It was, however, found

that the decomposition of benzidine sulphate by water or aqueous solutions does not take place in such a simple manner, since the addition of benzidine to a solution which was in equilibrium with benzidine sulphate caused a marked decrease of the sulphuric acid potential. Further investigation disclosed the existence of the *compounds* $[C_{12}H_8(NH_2)_2]_3,2H_2SO_4$ and $[C_{12}H_8(NH_2)_2]_2,H_2SO_4$ in addition to the well-known sulphate. By the aid of elements, in which the sulphuric acid potential was maintained constant in the manner indicated, the affinity of the reaction $KCl + \frac{1}{2}Na_2SO_4$ was estimated to be 210 cal. H. W.

The Term "Inversion." J. B. FERGUSON (*Science*, 1919, N.S.], **50**, 544—546).—The following terminology in inorganic chemistry is suggested. Changes such as the passage of rhombic to monoclinic sulphur, the equilibrium temperatures of which are fixed at fixed pressures, regardless of the complexity of the system, provided no solid solutions are formed, are examples of "inversion." Such reactions as the melting of sodium sulphate decahydrate, which occur, under a definite pressure, within a range of temperatures in presence of a third component, are cases of "transition." "Dissociation" is the name given to univariant changes when the compositions of all the phases can be represented by chemical formulæ. J. R. P.

Proportions of Chlorine and of Hydrogen which Limit the Explosion of Mixtures of these Gases. PAUL MATHIEU (*J. Physique*, 1917, **7**, 166—172).—If a mixture of hydrogen and chlorine is exposed to the radiation from the spark of an induction coil, explosion occurs only when the composition of the mixture is between the limits 91·9% of chlorine and 8·1% of hydrogen and 14·3% of chlorine and 85·7% of hydrogen. When exposed to the radiation of a magnesium flame, the explosive mixtures lie between the limits 90·2% of chlorine and 9·8% of hydrogen and 47·5% of chlorine and 52·5% of hydrogen. The different explosion limits are possibly due to the good conductivity of hydrogen for heat. CHEMICAL ABSTRACTS.

Hydrolysis of Esters of Polyhydric Alcohols. II. EIICHI YAMAZAKI (*J. Tokyo Chem. Soc.*, 1919, **40**, 667—680).—In this paper are given the experimental data obtained in connexion with the equation previously deduced for the hydrolysis of triacetin to glycerol (this vol., ii, 170). CHEMICAL ABSTRACTS.

Catalysis. VII. Catalysis in Heterogeneous Systems. NIL RATAN DHAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 570—575).—The velocity of solution of anhydrous ferric sulphate in water can be increased by the presence of reducing agents, such as stannous chloride or ferrous sulphate, but no satisfactory explanation of this phenomenon is forthcoming.

When 20% nitric acid in excess acts on copper at 18°, so that

the whole of the copper is dissolved, the action is accelerated by both ferrous and ferric salts, as well as by a number of other salts and compounds. The view hitherto held regarding the part played by ferrous salts in destroying nitrous acid needs to be modified, since it has been shown that nitrous acid is formed by the action of nitric acid on ferrous salts. Oxidising agents like hydrogen peroxide, potassium permanganate, chromic acid, etc., which destroy nitrous acid, retard the action of nitric acid on copper. Finally, there is a small group of substances which in very small concentrations exert a slight accelerating effect, whilst in large concentrations they have a retarding effect (compare T., 1917, **111**, 707). W. G.

The Effect of Surface Oxidation on some Metallic Catalysts. FRANK F. RUPERT (*J. Amer. Chem. Soc.*, 1920, **42**, 402—411).—The observation reported by Wigand (*Sitzungsber. Ges. Naturwiss. Marburg*, 1907, p. 33) that platinum foil which has been used as an electrode acquires an increased catalytic activity towards detonating gas (electrolytic hydrogen–oxygen mixture) has been confirmed by the author. The increased activity, however, is confined to the anode; it is due to surface oxidation, and can be induced by chemical means as well as by anodic polarisation. The surface oxidation probably consists in the formation of a film of surface-combined oxygen of atomic dimensions. Increase of catalytic activity by anodic polarisation was also found in the case of palladium and of gold; in the case of cobalt, a slight increase detected was probably due to increase of the active surface by etching. An estimation of the comparative order of magnitudes of the activities of the metals examined gives 50 : 1 for the ratio of palladium to platinum, 2000 : 1 for platinum to gold, and 200 : 1 for platinum to cobalt. The results obtained contradict Sackur's conclusions with regard to the effect of polarisation on the catalytic activity of metals (*A.*, 1906, ii, 261). E. H. R.

Do Simple Numerical Relationships Exist between the Linear Dimensions of the Atoms? MARIANO PIERUCCI (*Nuovo Cim.*, 1920, [vi], **19**, i, 109—115).—The author assumes that only at the absolute zero of temperature is it possible for the atomic volume to represent the true volume of the atoms. On this assumption, he calculates the cube root of the atomic volume at absolute zero for those elements which (1) have a known density in the solid state, and (2) have a coefficient of thermal expansion which either is known at low temperatures or is known and very small at ordinary temperatures. To this cube root he gives the name *atomic radius*. The necessary data are taken from Landolt's tables, and are known, in some instances only approximately, for twenty-nine elements. The results obtained appear to suggest that the atomic radii of all elements are integral multiples of one and the same length. T. H. P.

Electron Ring Model and the Electrical Moment of some Dipolar Molecules. LÉON SCHAMES (*Physikal. Zeitsch.*, 1920, **21**, 156—158. Compare this vol., ii, 172).—The electrical moment (M) of diatomic molecules is considered theoretically, and equations are developed by which this factor, and other factors connected with the structure of molecules, may be calculated. Calculations are carried out for the molecules of carbon monoxide, hydrogen chloride, water, and carbon dioxide, and the following values obtained; h is the distance between the two nucleii of effective charge number n_1 and n_2, respectively, and mass m_1 and m_2; r_1 and r_2 are the distances of the nuclei from the mechanical centre of gravity, and d_1 and d_2 their distances from the electron ring; a is the radius of the ring of n electrons, ω is the angular velocity of the electrons in the ring, which is calculated from the quanten equation $na^2\omega = kh/2\pi$, where the quanten number k for the second and third ring is equal to 2; x is the fraction of h where the electrical centre of gravity of the ring lies, and yh is the distance the electrical centre of gravity of the nucleus lies from the nucleus n, that is, $y = n_2/n$; l is the length of the dipole, and the other symbols have their usual meaning. Carbon monoxide, $P = 10{\cdot}07 \times 10^{-40}$, $Q = 10{\cdot}07 \times 10^{-40}$, $n_1 = 6$, $n_2 = 4$. $h = 0{\cdot}951 \times 10^{-8}$, $r_1 = 0{\cdot}4075 \times 10^{-8}$, $r_2 = 0{\cdot}5435 \times 10^{-8}$, $x = 0{\cdot}184$, $y = 0{\cdot}400$, $d_1 = 0{\cdot}175 \times 10^{-8}$, $d_2 = 0{\cdot}776 \times 10^{-8}$, $a = 0{\cdot}713 \times 10^{-8}$, $\omega = 4{\cdot}60 \times 10^{16}$, $l = 0{\cdot}205 \times 10^{-8}$, and $M = 9{\cdot}70 \times 10^{-18}$. Hydrogen chloride, $P - Q = 2{\cdot}7 \times 10^{-40}$, $n_1 = 7$, $n_2 = 1$, $h = 1{\cdot}31 \times 10^{-8}$, $r_1 = 0{\cdot}036 \times 10^{-8}$, $r_2 = 1{\cdot}274 \times 10^{-8}$, $x = 0{\cdot}0034$, $y = 0{\cdot}125$, $d_1 = 0{\cdot}0045 \times 10^{-8}$, $d_2 = 1{\cdot}3055 \times 10^{-8}$, $a = 0{\cdot}786 \times 10^{-8}$,

$$\omega = 3{\cdot}78 \times 10^{16},$$

$l = 0{\cdot}159 \times 10^{-8}$, $M = 6{\cdot}02 \times 10^{-18}$. Water, $P = 2{\cdot}21 \times 10^{-40}$, $Q = 1{\cdot}25 \times 10^{-40}$, $R = 0{\cdot}96 \times 10^{-40}$, $n_1 = 6$, $n_2 = 1$, $h = 0{\cdot}657 \times 10^{-8}$, $h = 0{\cdot}542 \times 10^{-8}$, $r_1 = 0{\cdot}0734 \times 10^{-8}$, $r_2 = 0{\cdot}796 \times 10^{-8}$, $x = 0{\cdot}027$, $y = 0{\cdot}250$, $d_1 = 0{\cdot}0177 \times 10^{-8}$, $d_2 = 0{\cdot}639 \times 10^{-8}$, $a = 0{\cdot}402 \times 10^{-8}$, $\omega = 14{\cdot}4 \times 10^{16}$, $l = 0{\cdot}146 \times 10^{-8}$, $M = 1{\cdot}87 \times 10^{-18}$. Carbon dioxide, $P = 9{\cdot}40 \times 10^{-40}$, $Q = 5{\cdot}83 \times 10^{-40}$, $R = 3{\cdot}57 \times 10^{-40}$, $n_1 = 4$, $n_2 = 6$, $h = 0{\cdot}708 \times 10^{-8}$, $h = 0{\cdot}262 \times 10^{-8}$, $r_1 = 0{\cdot}515 \times 10^{-8}$, $r_2 = 0{\cdot}325 \times 10^{-8}$, $x = 0{\cdot}90$, $y = 0{\cdot}75$, $d_1 = 0{\cdot}637 \times 10^{-8}$, $d_2 = 0{\cdot}071 \times 10^{-8}$,

$$a = 0{\cdot}485 \times 10^{-8},$$

$\omega = 9{\cdot}92 \times 10^{-16}$, $l = 0{\cdot}106 \times 10^{-8}$, $M = 8{\cdot}01 \times 10^{-18}$. J. F. S.

Twenty-sixth Annual Report of Committee on Atomic Weights. Determinations Published during 1918 and 1919. GREGORY PAUL BAXTER (*J. Amer. Chem. Soc.*, 1920, **42**, 327—333).—Papers published during 1918 and 1919 dealing with atomic weight determinations are summarised. E. H. R.

Arrangement of Electrons in the Elements of the Long Periods. RUDOLF LADENBURG (*Naturwiss.*, 1920, **8**, 5—11; from *Chem. Zentr.*, 1920, i, 315—316).—The arrangement of electrons postulated by Kossel (A., 1919, ii, 408) gives satisfactory results as far as scandium. For elements of higher atomic weight, how-

ever, it must be replaced by another conception, since it demands a definite prevalent valency, whilst the elements from titanium to zinc and from zirconium to cadmium exhibit a series of mobile valency stages, and, also, the maximal valency, so far as such can be spoken of, does not increase from member to member, but remains constant. Peculiar physical properties, such as magnetism of the elements and colour of the elementary ions, are associated with the change in chemical behaviour. Both properties are dependent on conditions under which the readily separable outermost valency electrons are already detached. Those elements which are paramagnetic and have small atomic volumes yield coloured, positively charged ions in the dissolved state and in glasses and precious stones. To account for the peculiar position of the elements of the series mentioned above, the author considers that the outermost zone of all the elements from titanium to zinc, and from yttrium to cadmium (except copper and silver), contains two electrons. The common metallic character of the majority of these elements, and the fact that they are at least positively bivalent in their heteropolar compounds, thereby find their expression. The sharp maxima of the atomic volumes of the alkali metals indicate that with them a new electron zone commences; this is certainly not the case with copper, silver, and gold, the atomic volumes of which lie near the minima, and are scarcely to be distinguished from the neighbouring elements. The new electrons of the elements titanium, vanadium, chromium, etc., must migrate into the interior of the outermost zone, but are supposed to form an intermediate zone between the two outer ones previously described, since they can participate in chemical reactions in the same manner as the electrons of the outermost zone, but have greater freedom of motion than these, and can also be separated singly; an explanation of the varying valency of these elements is thus given. In the cases of zinc and cadmium, in which the number of electrons in the intermediate zone is already increased to ten, a stable arrangement similar to that of the noble gases is postulated, so that an electron of this zone cannot be detached in exchange with other atoms. In the cases of gallium and indium, the new electrons take their place in the outer zones (as in the short periods), which in the corresponding rare gases (krypton and xenon) contain eight electrons. The assumption of the intermediate zones facilitates the understanding of the relationship between the colour of the ions and the periodic system. It is thereby assumed that the electrons of the intermediate zone, when the latter is incomplete and contains less than ten electrons, are more readily displaced by the energy of visible light, and, in accordance with Bohr's conception of emission and absorption, absorb the corresponding energy and pass to a path of greater energy. Absorption in the ultra-violet must be accomplished by electrons of other, more complete zones. Although an analogy must exist between the colour of the ions and the variable valency, since each property is ascribed to the looseness of the attachment

of the electrons in the incomplete intermediate zone, a complete agreement between these properties is not to be expected. The connexion between colour and ability to form compounds depends on the amounts of energy which are required for the absorption of light on the one hand, and for the production of another degree of combination on the other. The quantities of energy are related in the same manner as the resonance potential and ionisation tension in the line spectra of metals. Doubtless, coloured compounds can exist in which the intermediate zone is absent, but mobility of the electrons is due to other influences. The simultaneous appearance of colour in the ions and of paramagnetism in the periodic scheme indicates that the latter is also caused by the electrons of the intermediate zone, although it is acknowledged that the latter phenomenon is but little understood. The distinctive characteristics of the electrons of the magnetic elements are still less obvious, and are not expressed in the author's scheme. The latter is, however, only to be regarded as a preliminary conception. H. W.

New Periodic Relationship between the Atomic Weights of the Chemical Elements. KARL FEHRLE (*Physikal. Zeitsch.*, 1920, **21**, 162—166. Compare A., 1918, ii, 296).—A theoretical paper in which, on the basis of the quantum theory, an expression is evolved whereby the atomic weight of the elements may be calculated. The calculation is based on the atomic model previously described by the author (*loc. cit.*). The atomic weight is calculated by means of the formula $A = \Sigma_1^n \sqrt[7]{67 \cdot 7 + (n-1)16 \cdot 59}$, where n is the number of sheaths in the atom. The calculated atomic weights run parallel with the experimental values, and the difference between the two is a periodic function of the atomic weight. The cause of this periodic function is to be found in the characteristic vibrations of the molecule in relationship to those of its atoms. J. F. S.

Inter-relationship of the Chemical Elements. HAWKSWORTH COLLINS (*Chem. News*, 1920, **120**, 169—170).—The author has picked out nine pairs of elements, the sum of the atomic weights of each pair of which approximate to that of vanadium; six pairs, the sum of the atomic weights of which approximate to that of chromium; and eight pairs, the sum of the atomic weights of which approximate to that of manganese. In these tables, three sets of coincidences are apparent: (i) The sum of the valencies of each pair is equal to the valency of the element under consideration in seventeen cases out of twenty-three. (ii) The sum of the valencies of each pair is odd or even according as the valency of the element under consideration is odd or even. (iii) The sum of each pair of atomic weights is greater than the integer which is nearest to the atomic weight of the element under consideration in twenty cases out of twenty-three, when the atomic weight of oxygen is taken as sixteen, and is less than the same in nineteen cases out

of twenty-three when hydrogen is taken as the unit. It is shown that the probability that the first coincidence is due to chance is one to several billions, that the second is a chance or accident is one to eight millions, and that the third is a chance or accident is one to four thousand millions. The author concludes, therefore, that these relationships are due to some general similarity in the formation of the elements. [See also A., 1919, ii, 106.]

J. F. S.

Dependence of the Valency Number on Temperature. III. The Systematic Doctrine of Affinity. X. WILHELM BILTZ (*Zeitsch. anorg. Chem.*, 1919, **109**, 132—144. Compare A., 1915, ii, 440, 465, 466).—A theoretical paper in which the dependence of the valency exercised by various elements at different temperatures is considered. The dissociation of the higher chlorides of gold, platinum, iridium, and vanadium, the oxides of iron, uranium, and lead, the crystalline hydrates of uranyl nitrate and certain sulphides is discussed, and the dissociation represented as valency isobars. From this consideration, it is shown that the valency isobars are steeper the lower the temperature of the starting point. This rule, however, is not absolute, for when substances which have dissimilar constitutions are considered, it fails entirely. The constitutive influences are considered in connexion with the metal ammines. The temperature range over which the ammines of the chlorides of the metals manganese, iron, cobalt, and nickel are stable is tabulated. In the case of the hexammines, that of nickel iodide has the greatest temperature range of existence (177·5°), and that of manganese chloride the least. The order of existence increases from manganese to iron, cobalt, and nickel, and from chloride to bromide and iodide. In the case of the diammines, the range of existence increases from chloride to bromide, and falls again to the iodide to a value lower than that for the chloride; it also increases from manganese to iron, and then falls to cobalt and nickel. It is found in the monammines that the existence range falls from chloride to iodide and from manganese to nickel. J. F. S.

Calculation of the Chemical Constants of Polyatomic Gases from the Planck Theory of Probabilities. LÉON SCHAMES (*Physikal. Zeitsch.*, 1920, **21**, 156—159. Compare this vol., ii, 172).—It is shown that the strict calculation from the Planck probability theory leads to the same result as the Sackur-Tetrode calculation (*loc. cit.*). It is shown that $\sqrt[3]{PQR} = 0{\cdot}94 \times 10^{-40}$ for water according to the Sackur-Tetrode calculation, but from the rotation spectrum, according to Planck's first theory, the value is $1{\cdot}38 \times 10^{-40}$, and from the Planck second theory $2{\cdot}48 \times 10^{-40}$. No reason can, as yet, be given for the discrepancy. J. F. S.

Graphic Mixture Calculations. WA. OSTWALD (*Chem. Zeit.*, 1920, **44**, 241—242).—When it is required, from two or more

materials containing two or more constituents in known proportions, to produce another mixture containing the same constituents in other proportions, the calculation can be greatly simplified by the use of the graphic method. In more complicated cases, an exact solution of the problem may be impossible, and the graphic method then affords a ready means of obtaining an approximate solution. E. H. R.

Measurements of the Volume of the Mercury Meniscus. J. PALACIOS (*Anal. Fis. Quim.*, 1919, **7**, 275—295).—Exact determinations have been made of the volume occupied by the meniscus of mercury in glass tubes 5, 6, 7, 8, 9, 10, and 11 mm. in diameter, and with heights of meniscus varying by 0·1 mm. from 0·1 mm. to 2·1 mm. The author draws attention to a constant appreciable difference between his results and those of Scheel and Heuse (*Ann. Physique*, 1910, **33**, 291), and suggests that an error of 0·04 mm. for the radius of the tube used by Scheel and Heuse would account for the discrepancies. W. R. S.

Apparatus for the Extraction of Liquids. KURT BRAUER and ERWIN W. EBERT (*Chem. Zeit.*, 1920, **44**, 214).—An apparatus of the Soxhlet type is described for the extraction of a liquid with a solvent of greater density. In place of the usual siphon of the apparatus, a tube is provided extending upwards from the bottom of the main cylinder and entering the side (vapour) tube at about two-thirds the height of the latter. As the heavy solvent collects below the liquid undergoing extraction, it flows gradually back through the side-tube into the extraction flask. A tap is provided between the cylinder and stem of the apparatus. W. P. S.

Lecture Experiment on Combustion. A. PRICE (*Chem. News*, 1920, **120**, 149—150).—A Bunsen burner is made with a long, wide glass tube in place of the usual metal tube, and a little above the top of the tube a wire is clamped at right angles to it. The gas is turned on so that a mixture of coal-gas and air ascends the tube, as in the ordinary Bunsen burner. By carefully lowering a small flame on to the wire, with possibly a little adjustment of the gas supply, the gas can be made to burn indefinitely from the top of the wire with a very pale blue, luminous flame. The flame can similarly be made to burn from a small, rounded object, such as a bullet, suspended above the tube by a fine wire. The continuance of the phenomenon depends on the mixed gases coming up the tube at a certain velocity, too great for combustion to take place at the end of the tube. The presence of the wire or small object lowers the velocity sufficiently to permit the gases to burn. When the velocity is lowered sufficiently by cutting off the gas supply, the flame strikes back to the jet at the bottom of the tube. E. H. R.

Inorganic Chemistry.

The Purification of Liquefied and Compressed Gases for Laboratory Purposes. L. MOSER [and, in part, W. FOLTZ] (*Zeitsch. anorg. Chem.*, 1920, **110**, 125—142).—An account is given of the impurities likely to be present in those gases which are supplied commercially in cylinders, and of the best means for purifying the gases. Carbon dioxide, which is obtained commercially by heating a metal hydrogen carbonate solution, contains 1—2% of impurity. It can be completely freed from oxygen by passing it at a rate of 4 to 6 litres per hour through a paste of chromium acetate, and then through a 15% solution of titanous chloride acidified with hydrochloric acid, or by passing over red-hot copper at 4 to 10 litres per hour. Carbon monoxide can be removed by passing the gas over asbestos carrying finely divided cuprous oxide at 700—800°, hydrogen sulphide by copper sulphate on pumice stone, and sulphur dioxide by a solution of potassium permanganate. Commercial nitrogen, prepared by the Linde process, has only to be freed from traces of oxygen. The best wet absorbent is copper gauze in ammonium carbonate solution, the gas being subsequently passed through concentrated sulphuric acid to absorb ammonia. It can finally be passed over copper asbestos at 700—800° to remove the last trace of oxygen. Electrolytic hydrogen is practically pure, but that prepared from water gas by the Linde process may contain air, oxides of carbon, and sometimes arsine. Further, through the action of the carbon monoxide on the steel cylinder under pressure, iron pentacarbonyl is formed, and the hydrogen may contain more than 3% of it. Owing to the difficulty of removing this impurity or the carbon monoxide formed by its decomposition, such hydrogen is unsuitable for laboratory use. Commercial oxygen, prepared by the Linde process, contains only traces of nitrogen, which cannot be removed by chemical means, and a trace of carbon dioxide which can be removed by soda-lime. Electrolytic oxygen may contain as much as 4% of hydrogen, which can be burnt to water by passing the gas over heated platinised asbestos. Commercial chlorine, generally of electrolytic origin, can be freed from air and oxides of carbon by liquefying in a tube immersed in a mixture of ether and carbon dioxide and redistilling, and commercial sulphur dioxide can be purified in the same way, although it is pure enough for most purposes. Commercial ammonia contains about 2% of impurity, consisting of water and organic substances, such as pyridine, methylamine, and pyrrole. The gas can be dried by means of lime or soda-lime, but the organic impurities are difficult to remove. E. H. R.

Determination of the Boiling Point of Sulphur by means of the Nitrogen Thermometer. P. CHAPPUIS (*Bur. Int. Poids. Mes.*, 1917, *Mem.* **16**, 44 pp.).—The b. p. of sulphur at normal

pressure, determined by measuring the increase of pressure at constant volume of nitrogen (prepared from a solution of sodium nitrite, ammonium sulphate, and potassium chromate, and washed with a mixture of potassium dichromate and sulphuric acid and then with potassium hydroxide) in a silica bulb of capacity approximately 247 c.c., was found to be 444·60° on the thermodynamic scale.

The original paper should be consulted for details of the apparatus employed and the corrections made.

CHEMICAL ABSTRACTS.

Action of Hydroxylamine on Sodium Tetrathionate. A. GUTMANN (*Ber.*, 1920, **53**, [*B*], 444—446).—In acid solution, hydroxylamine oxidises the sulphite residue in tetrathionic acid to sulphuric acid, and is itself reduced to ammonia, $H_2S_4O_6 + NH_2{\cdot}OH + H_2O = 2H_2SO_4 + 2S + NH_3$. In alkaline solution, on the other hand, the loosely combined oxygen atom of the tetrathionate oxidises hydroxylamine to nitrous or nitric acid, $Na_2S_4O_6 + 2NH_2{\cdot}OH + 3NaOH = 2Na_2S_2O_3 + NaNO_2 + 3H_2O + NH_3$.

H. W.

The Decomposition Equilibrium of Nitrosyl Bromide and the Proof of (the Formation of) the Tribromide, $NOBr_3$. MAX TRAUTZ and VASANJI P. DALAL (*Zeitsch. anorg. Chem.*, 1920, **110**, 1—47).—A continuation of previous work (A., 1918, ii, 162). The equilibrium between nitric oxide, bromine, and their reaction products was studied between −15° and 330° by the method previously described (compare Trautz and Wachenheim, A., 1917, ii, 74), with bromine pressures between 13 and 500 mm., and nitric oxide pressures between 28 and 900 mm. Equilibrium is attained very rapidly, and the reaction is the most rapid which has yet been studied. For low bromine pressures, below 50 mm., and at temperatures above 140°, the amount of the tribromide formed appears to be negligible, and the reaction $2NO + Br_2 \rightleftharpoons 2NOBr$ can be regarded as of the third order. As is to be expected from the small heat of reaction, the reaction is more rapid than the formation of nitrosyl chloride. The velocity constant is, at −15°, $k = 1{\cdot}1 \times 10^{-10}$.

An independent proof of the existence of nitrosyl bromide and nitrosyl tribromide was obtained from an investigation of the fusion-point diagram of the reaction products of bromine and nitric oxide. The fusion curve shows a eutectic of bromine and nitrosyl tribromide, a maximum at −40° corresponding with $NOBr_3$, a second eutectic of $NOBr_3$ and NOBr in the neighbourhood of −60°, and a second maximum corresponding with NOBr at about −55°. Nitrosyl tribromide was found to be a brownish-black, almost opaque liquid which begins to boil, with partial decomposition, at about 32°. It has $D_4^{20} = 2{\cdot}637$, which agrees closely with Landolt's value, 2·628 at 22·6°. The fusion diagram does not confirm or exclude the existence of nitrosyl dibromide

among the products. The heats of formation of the mono- and tri-bromide were calculated from measurements made of their heats of reaction in aqueous solution with potassium hydroxide. The significance of the results obtained cannot be exactly estimated, because the extent of decomposition of liquid NOBr and $NOBr_3$ is unknown, but probably the heat of formation of NOBr is between 9000 and 10,500 cal., and of $NOBr_3$ between 22,000 and 27,000 cal., at 22°. The results obtained for the equilibrium constants and for the heats of formation agree, in general, with theory. It is concluded that, in liquid mixtures of the components at low temperatures, the principal product is nitrosyl tribromide, in gaseous mixtures rich in bromine at moderate temperatures, nitrosyl dibromide, and under other conditions, nitrosyl bromide or its decomposition products.

E. H. R.

War Experiences in the Manufacture of Nitric Acid and the Recovery of Nitrous Fumes. JAMES WALKER (T., 1920, **117**, 382—389).—A lecture delivered before the Chemical Society on December 18th, 1919.

Interaction of Phosphorus Haloids and Arsenious and Arsenic Compounds. NAGENDRA NATH SEN (*J. Proc. Asiatic Soc. Bengal*, 1919, **15**, 263—265).—When a few drops of phosphorus trichloride are added to an aqueous solution of arsenious oxide, the solution turns yellow, then opaque-brown, and finally a copious precipitate of arsenic is thrown down. The arsenic is amorphous, apparently a new allotropic form, insoluble in carbon disulphide. The reaction does not take place when phosphorous acid is used or when the phosphorus trichloride is first dissolved in water. With phosphorus tribromide and tri-iodide, the same reaction takes place, but more slowly, and in the latter case the precipitate is contaminated with red phosphorus. Unlike the trichloride, the tribromide and tri-iodide still bring about the reaction if they are first dissolved in water. It appears, therefore, that an intermediate compound is first formed when the phosphorus haloid dissolves in water, but that, in the case of the trichloride, this intermediate compound is more rapidly decomposed than in the cases of the other haloids. The reduction, which takes place with both arsenites and arsenates, is brought about by the intermediate compound. The reaction is very delicate, and with phosphorus trichloride the presence of 0·000075 gram of arsenic per c.c. can be detected. Antimonious and antimonic compounds do not give the reaction. The course of the reduction is probably given by the equation $As_2O_3 + 3PCl_3 + 9H_2O = 2As + 3H_2PO_4 + 9HCl$.

E. H. R.

Coagulation of Metal Sulphide Hydrosols. II. Influence of Temperature on the Rate of Coagulation of Arsenious Sulphide Hydrosols. JÑANENDRA NATH MUKHERJEE (T., 1920, **117**, 350—358).

Charcoal before the War. I. WILDER D. BANCROFT (*J. Physical Chem.*, 1920, **24**, 127—146).—A theoretical paper in which the composition and structure of various forms of charcoal are discussed. J. F. S.

Some Properties of Charcoals. H. E. CUDE and G. A. HULETT (*J. Amer. Chem. Soc.*, 1920, **42**, 391—401).—When the density of charcoal is determined by the water immersion method, a gradual increase in weight of the immersed charcoal is observed, the maximum weight only being reached after many days. The same occurs when other liquids, such as carbon disulphide, benzene, or carbon tetrachloride, are used instead of water, and in each case the final density found for the charcoal is different. Quantitative experiments were made with a sample of cocoanut charcoal, 18—20 mesh, and the maximum densities found were: with water, 1·854; with carbon disulphide, 1·984; with benzene, 1·797; and with carbon tetrachloride, 1·647. The change in weight of the immersed charcoal with time is due to the progressive penetration of the liquid into the charcoal, rapidly at first, then more slowly. The rate of penetration and the final density found appear to vary in proportion to the surface tension and inversely with the viscosity of the liquid. The smaller the size of grain of the charcoal, the greater is the density found, and with the smallest grains obtainable, 0·001 mm. in diameter, using water as the liquid, the final density 1·900 was obtained. High pressure causes rapid penetration, and the 18—20-mesh charcoal in water under 8600 atm. gave a density of 1·902 in the course of a comparatively short time. E. H. R.

Activation of Wood-charcoal by Heat Treatment. JAMES C. PHILIP, SYDNEY DUNNILL, and OLIVE WORKMAN (T., 1920, **117**, 362—369).

Oxidation of Carbon Monoxide. KARL HOFMANN (D.R.-P 307614; from *Chem. Zentr.*, 1920, ii, 446).—The process is effected by chromic acid solution to which mercuric oxide has been added. The presence of the latter substance so accelerates the oxidation of carbon monoxide that this gas can be removed from its mixtures with air and other gases with sufficient rapidity for analytical and hygienic purposes. H. W.

Carbonyl Chloride. E. PATERNÒ and A. MAZZUCCHELLI (*Gazzetta*, 1920, **50**, i, 30—53).—The carbonyl chloride was prepared by the action of fuming sulphuric acid on carbon tetrachloride, and was purified by distillation with the help of a dephlegmator maintained at constant temperature. A special apparatus was designed for storing the chloride obtained and for delivering small amounts of it as required.

The density of liquid carbonyl chloride, measured by means of a dilatometer with a graduated capillary tube at temperatures

between $-15{\cdot}4^\circ$ and $+59{\cdot}9^\circ$, is expressed well by the formula $D = 1{\cdot}4264 - 0{\cdot}002326t$, t being in degrees Centigrade.

Determinations have been made of the orthobaric density of liquid carbonyl chloride and its vapour by means of Ter-Gazarian's modification (A., 1906, ii, 423) of Young's process, the temperatures employed lying between 60·3° and 181·6°. In accordance with the rectilinear diameter law of Cailletet and Mathias, the sum of the densities of the liquid and vapour varies very nearly linearly with the temperature, the maximum divergences being less than 0·3%. The whole of the results agree well with the expression $1{\cdot}4277 - 0{\cdot}00214t$, whilst for temperatures above 111°, for which the diameter is more certainly rectilinear, the formula $1{\cdot}4380 - 0{\cdot}0022t$ holds.

Comparison of the orthobars of carbonyl chloride and *n*-pentane (see Young, T., 1897, **71**, 455) gives for the critical temperature of carbonyl chloride the value 187°, which should be accurate to within 1—2°. The two expressions given above then lead to the respective values 0·5137 and 0·5133 for the critical density. The conclusions arrived at by Young from considerations based on the law of the rectilinear diameter show that for carbonyl chloride this diameter is convex towards the axis of temperature, and also lead to the provisional value 51·5 atmos. for the critical pressure. According to Mathias, the extrapolated density at absolute zero is three times the critical density, but for carbonyl chloride, such extrapolated density, calculated in accordance with Mendeléev's formula, is almost exactly four times the critical density.

Measurements of the surface tension of carbonyl chloride have been made by means of Ramsay and Shields' method (T., 1893, **63**, 1094), the values obtained for $\gamma = ga^2(d - \sigma)/2$ being 19·51 at 16·7°, 17·10 at 34·5°, and 15·42 at 46·1°. The so-called molecular tension, $G = \gamma(M/S)^{\frac{2}{3}}$, has the mean value 2·05, which agrees well with the value 2·12 given by Ramsay for non-polymerised compounds.

Various series of measurements of the vapour pressure at temperatures ranging from about -23° to $+25^\circ$ have been made, the results being in satisfactory agreement with the formula $\log p = 7{\cdot}5995 - 1326/T$, p being the absolute pressure in mm. of mercury at the latitude of Rome and T the absolute temperature. This formula indicates the boiling point of carbonyl chloride to be 8·02°/760 mm., whereas Beckmann (*Zeitsch. anorg. Chem.*, 1907, **55**, 371) found 8·2°/756 mm.

Berthelot's statement that carbonyl chloride dissolves unaltered to the extent of 2—3 vols. in water, and that it reacts with the latter only slowly, has been contested by recent authors (compare Grignard and Urbain, A., 1919, ii, 340). The authors find that the chloride cannot exist for an appreciable time in contact with pure water, but that the products, carbon dioxide and hydrochloric acid, which it forms with the water hinder further action; in the case of gaseous carbonyl chloride, the carbon dioxide forms an inert separating layer at the surface of the liquid, whilst with

liquid carbonyl chloride it is saturation with hydrogen chloride of the water in immediate contact with the liquid to which retardation of the reaction is due. The action is therefore dependent essentially on diffusion.

Retardation of the reaction between carbonyl chloride and water is caused by acids in general. Attempts made to measure the velocity of the reaction in presence of sulphuric acid by measuring the volumes of carbon dioxide evolved in different periods of time led to irregular results, but showed that the reactivity of sulphuric acid solutions with carbonyl chloride diminishes continuously with increase in the concentration of the sulphuric acid and with fall in the temperature. No hypothesis is advanced to explain this effect of acids, which is due, undoubtedly, to a true retardation of the reaction, and not to a displacement of the equilibrium.

The reaction between carbon tetrachloride and fuming sulphuric acid is not limited to that expressed by the equation $CCl_4 + 2SO_3 = S_2O_5Cl_2 + COCl_2$, since in presence of excess of the hot fuming acid, the reaction $CCl_4 + 4SO_3 = 2S_2O_5Cl_2 + CO_2$ takes place.

If kept at a temperature below 0°, liquid carbonyl chloride *absorbs gaseous chlorine in large proportions.* At −15° and under the ordinary pressure, a golden-yellow liquid containing 28·3% of free chlorine is formed; the vapour pressures of this liquid at different temperatures exhibit satisfactory agreement with the law stating that, in mixtures of similar and non-polymerised liquids, the partial pressure of any component is equal to the pressure of the pure component multiplied by its molecular percentage in the mixture.

Carbonyl chloride is absorbed in considerable proportions by heavy lubricating oils, from which it is expelled rapidly and almost completely by a current of air. T. H. P.

The Production of Helium and Neon in Discharge Tubes containing Hydrogen. ARNALDO PIUTTI and ETTORE CARDOSO (*Gazzetta*, 1920, **50**, i, 5—23).—The authors have carried out a number of experiments on the action of the discharge between aluminium electrodes on hydrogen prepared by the electrolysis of dilute sulphuric acid and carefully purified. By means of the spectroscope employed, the neon contained in 0·05 c.c. of air could be detected with ease. After the subjection of the hydrogen to the action of the discharge, the gas was burnt in oxygen prepared by heating potassium permanganate and carefully purified before use; the burnt gases were extracted and purified, and the residue examined spectroscopically. The apparatus used is briefly described. The pressure maintained during the discharge, which occupied from one to twelve hours, varied in different experiments between 0·1 mm. and 3 mm., the temperature prevailing being also varied in different cases.

In no single case was the formation of helium or neon in the tubes detectable, this result being in agreement with that of Strutt,

(A., 1914, ii, 201) and in contradiction to that of Collie, Patterson, and Masson (A., 1914, ii, 847; compare Baly, Annual Report, 1914, 45). T. H. P.

The Solubility of Potassium Bromide in Bromine Water. Alfred Francis Joseph (T., 1920, **117**, 377—381).

Formation of Mixed Crystals of Potassium and Ammonium Nitrates at the Ordinary Temperature. Caillart (*Bull. Soc. franç. Min.*, 1918, **41**, 21—30; from *Chem. Zentr.*, 1920, i, 358).—The work is an extension of that of Wallerant (A., 1906, ii, 151), who has investigated the formation of the mixed crystals from the molten salts. The method suffers particularly from the drawback that the crystals remain in a metastable condition outside the limits of their stability. The author has therefore investigated the crystals deposited from aqueous solutions at a constant temperature, 17°. Difficulties are encountered owing to the great disparity in the solubilities of the salts and to the poor development of the mixed crystals rich in ammonium nitrate, which almost prevents measurement. Crystallographic methods are therefore supplemented by optical ones. The solubility curves of mixtures of the two salts, and the graphs showing the relationship between the composition of the mixed crystals and that of the mother liquors, have been studied in particular, and are found to be composed of three segments corresponding with three types of mixed crystals: (1) rhombic crystals of the potassium nitrate type containing 0—17·2 molecules of ammonium nitrate per 100 molecules of mixture, (2) monoclinic crystals with 55—94·5 molecules of ammonium nitrate per 100 molecules of mixture, and (3) rhombic crystals of the ammonium nitrate type with 98—100 molecules of ammonium nitrate per 100 molecules of mixture. Two types of mixed crystals separate at each concentration, corresponding with the two points of intersection of the curves.

H. W.

Influence of Various Metals on the Decomposition of Sodium Amalgam by Water. Erich Müller and Alfred Riedel (*Zeitsch. Elektrochem.*, 1920, **26**, 104—109).—The rate of decomposition of water by 0·2% sodium amalgam in the presence of metallic and other substances has been determined. The amalgam (80 grams) was rapidly stirred with 50 c.c. of water and a piece of the metal in question, and the hydrogen collected and measured. The experiments were carried out with ferro-molybdenum, cast iron, wrought iron, iron carbide, silicon, ferro-silicon, ferro-vanadium, ferro-tungsten, chromium, platinum, palladium, iridium, nickel, cobalt, manganese, tantalum, graphite, and ferric oxide. It is shown that the iron alloys of molybdenum, vanadium, tungsten, and chromium have a very strong catalytic action on the process. This action depends on the increase in the surface of the amalgam due to the solution, and subsequent separation of the metals. The possibility of applying this action to

the manufacture of sodium hydroxide by the mercury electrode process is considered, and it is shown that if the finely divided catalyst can be entirely removed from the mercury at the end of the process, then it will be advantageous to add the catalyst to the electrolyte in the mercury cells, but if it is not possible to entirely remove the catalyst, then the total current will not be used in the formation of amalgam, but a portion will be used in the liberation of hydrogen. J. F. S.

Behaviour of Magnesium Nitride towards Carbon Monoxide and Carbon Dioxide. FR. FICHTER and CHRISTOPH SCHÖLLY (*Helv. Chim. Acta*, 1920, **3**, 298—304).—The statement of Briegleb and Geuther (1862) that magnesium nitride reacts with carbon monoxide and carbon dioxide to give magnesium oxide, cyanogen, and carbon, and, in the latter case, nitrogen also, is erroneous. Quantitative experiments show that the decomposition of the freshly prepared nitride at 1250° in a stream of the respective gases is expressed by the following equations: $Mg_3N_2 + 3CO_2 = 3MgO + 3CO + N_2$ and $Mg_3N_2 + 3CO = 3MgO + N_2 + 3C$. Carbon monoxide causes no change at 750°, and reacts less readily than carbon dioxide. The reactions are considered to follow on the dissociation of the nitride, which was shown to be almost complete at 1500°. Aluminium nitride, which dissociates much less readily (Fichter and Oesterheld, A., 1915, ii, 168), is oxidised by carbon dioxide at 1300° only to the extent of 89%. Briegleb and Geuther's statement may have been due to confusion of hydrocyanic acid with cyanogen, since the authors observed a transient odour of the former from the product of the action of carbon monoxide on magnesium nitride. It is suggested in explanation of this that magnesium cyanide may have been produced to a slight extent by a reaction analogous to that by which calcium nitride is converted into the cyanide by the action of carbon and nitrogen. J. K.

The Reactions of the Metallurgy of Zinc. M. LEMARCHANDS (*Compt. rend.*, 1920, **170**, 805—807).—From a study of the interaction of zinc oxide and carbon in an atmosphere of nitrogen, it is shown that zinc oxide is readily reduced directly by carbon without the necessary intermediate formation of carbon monoxide. The amount of carbon entering into the reaction is intermediate between the amounts necessary for the two possible actions $ZnO + C = Zn + CO$, $2ZnO + C = 2Zn + CO_2$. This is explained on the grounds that the reduction of zinc oxide by carbon monoxide, $ZnO + CO = Zn + CO_2$, takes place with a velocity superior to that of the reduction of carbon dioxide by carbon. This is possible, since the first action commences at 350°, and the second only at 400°. Further, for any given temperature, the vapour pressure of zinc oxide is much greater than that of carbon. W. G.

Lead Chromate. MAX GRÖGER (*Zeitsch. anorg. Chem.*, 1919, **109**, 226—234).—When lead acetate is treated with an

valent quantity of potassium chromate, a slightly basic lead chromate is precipitated, the relationship between lead oxide and chromic acid being represented by $PbO:CrO_3::1·104:1$; if, however, 20 c.c. of *N*-potassium chromate are added to 19 c.c. of *N*-lead acetate, a light yellow precipitate is produced which, on stirring, changes to an orange-yellow, crystalline precipitate of normal lead chromate. When 40 c.c. of *N*-lead acetate are mixed with 10 c.c. of *N*-potassium chromate, and the mixture evaporated to dryness on the water-bath and then washed with hot water, a basic lead chromate of the composition $PbO,PbCrO_4$ is obtained. Rubbing 2 grams of normal lead chromate with 30 c.c. of *N*-potassium acetate solution, evaporating to dryness on a water-bath, and then washing with water, yields a double lead potassium chromate, $2PbCrO_4,K_2CrO_4,H_2O$. J. F. S.

Copper Silicon Alloys. A. SANFOURCHE (*Rev. Met.*, 1919, **16**, 246—256; from *Chem. Zentr.*, 1920, i, 409).—The alloys were prepared from electrolytic copper containing only 0·00007% of iron, and crystalline silicon, which after treatment with nitric and hydrofluoric acids left only 0·52% of residue and was free from iron; in spite of this, however, the alloys contained iron derived from the tubes, which seldom exceeded 0·25% in amount. The preparation of the alloys, the analytical methods, and the apparatus are shortly described, whilst the phase diagram and the results of microscopical and chemical investigation of the alloys are fully discussed. Rudolfi (A., 1907, ii, 352) has attributed the observed maximum (12·10% Si) to the formation of a compound, Cu_3Si (Cu = 87·04%, Si = 12·96%), but the difference in the silicon content exceeds the experimental error, whilst, also, the accuracy of his curve is greatly affected by the small number of alloys investigated. The formula $Cu_{13}Si_4$ (Cu = 87·91%, Si = 12·09%), on the other hand, is in good agreement with the results obtained. The effect of this compound and of Rudolfi's substance, $Cu_{19}Si_4$, on the formation of β- and γ-crystals is considered in the light of the phase diagram, and the possibility of the assumption of solid solutions instead of definite compounds is discussed. Since it is impossible to alloy more than 12·10% of silicon with copper, all the formulæ of copper–silicon alloys requiring a higher silicon content are to be deleted from the literatnre. H. W.

Amalgams. GIOVANNA MAYR (*Nuovo Cim.*, 1920, [vi], **19**, i, 116—128).—The authoress gives a brief summary of previous work on the constitution of amalgams, and from the results of her own experiments, not described in detail, the following conclusions are drawn. When the chemical constitution of an amalgam is known, determination of the *E.M.F.* of a concentration cell furnishes a means of deducing the ratio between the concentrations of the two amalgams forming the cell. During the passage of a current through an amalgam, the metal dissolved in the mercury is transported towards the anode, that is, in the direction of the negative current. As regards such transport, no appreciable distinction is

evident (1) between metals, such as thallium, which give rise to compounds with the mercury, and those, such as zinc, which dissolve as such in mercury, or (2) between metals, such as sodium and potassium, which increase the resistance of the mercury, and those, such as zinc, which diminish the resistance. Thus, in contradiction to Lewis's view (compare Lewis, Adams, and Lanman, A., 1916, ii, 76), such transport of the metal does not appear to be related to the increase or decrease of the resistance of the mercury produced by dissolution of the metal. Increase in the resistance of mercury may depend on the specific resistance of mercurides formed by the dissolved metal. T. H. P.

Colourless Variety of Mercuric Iodide. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1920, **109**, 213—214).—A colourless variety of mercuric iodide may be obtained as follows: a quantity (10—15 grams) of mercuric iodide is placed in a long tube, sealed at one end and connected with a large vessel at the other, and heated at 300—350°. The pressure is suddenly reduced to 0·1 atm., when mercuric iodide condenses in the large vessel as a white snow, which in a few seconds becomes rose-coloured, and in a few minutes has changed to the stable vermilion form of mercuric iodide. If the large vessel is previously cooled, the white form may be preserved for longer periods. The yellow variety of mercuric iodide becomes colourless at the temperature of liquid air. J. F. S.

The Solubility of Mercuric Oxide in Sodium Hydroxide Solutions. G. FUSEYA (*J. Amer. Chem. Soc.*, 1920, **42**, 368—371). —To determine whether a compound can possibly be formed through the interaction of mercuric oxide and sodium hydroxide, solubility determinations of the former were made in sodium hydroxide solutions of different concentrations at 25°. The solubility curves, in which concentration of mercuric oxide is plotted against sodium hydroxide and hydroxyl-ion concentrations, respectively, when extrapolated to zero concentration of hydroxide or hydroxyl ion, give a value for the solubility of mercuric oxide considerably above the normal solubility in pure water. It is considered probable that the normal solubility is that of the red form of the oxide, whilst the extrapolated value represents that of the more finely divided yellow form. The steady increase of the solubility of mercuric oxide as the concentration of sodium hydroxide increases indicates that the hydrated oxide functions as a very weak acid. The ionisation constant of the first hydrogen of mercuric acid, H_2HgO_2, is calculated to be $1\cdot7\times10^{-15}$. E. H. R.

Scandium. II. JAN ŠTĚRBA-BÖHM (*Bull. Soc. chim.*, 1920, [iv], **27**, 185—195. Compare A., 1914, ii, 565).—A study of scandium fluoride and certain of its double salts. Scandium fluoride, as prepared by Crookes's method (compare A., 1908, ii, 695), is not pure, because of the absorption of impurities during the precipitation. The fluoride may be obtained in a pure state

y the action of hydrofluoric acid on scandium oxide, the product eing finally heated at 150—180° to remove any free hydrogen uoride. Fluoroscandic acids do not exist in the free state, but hree ammonium scandifluorides were prepared. The ammonium candifluoride, $(NH_4)_3ScF_6$ (compare Meyer, A., 1914, ii, 369), ndergoes hydrolysis in water, giving first the *compound*, $NH_4)_2ScF_5$, quadratic crystals, and then the *compound*, $NH_4)ScF_4$, as a *microcrystalline* powder. The first compound is nly obtained by hydrolysis in the presence of ammonium fluoride; ı warm or cold water alone the second compound is always btained.

A small quantity of a crystalline *silver scandifluoride* was btained by dissolving scandium fluoride in a concentrated soluion of silver fluoride. W. G.

Light Reactions of Cerium Dioxide. CARL RENZ (*Zeitsch. norg. Chem.*, 1920, **110**, 104—106).—Pure cerium dioxide, which as a pale yellow colour, is unaffected by light, but if mixed with small quantity of praseodymia or terbia it becomes lightensitive. Such a mixture, which has a slightly reddish-yellow olour, when exposed to sunlight becomes bluish-grey, but in the ark its original colour is restored. In the cerite earths, cerium s known to have an oxidising influence on praseodymia, and pparently in sunlight this influence becomes emphasised. Disussing the position of the rare earth metals in the periodic system f the elements, the author expresses the view that, in the buildng up of the system, these elements are the counterpart of the ransition members of the radioactive series in the degradation of he system. E. H. R.

The Rare Earths. X. The Purification and Atomic Veight of Samarium. A. W. OWENS, C. W. BALKE, and H. C. KREMERS (*J. Amer. Chem. Soc.*, 1920, **42**, 515—522).—The amarium material used for these experiments was obtained from he Welsbach Mantle Co., and consisted of rare earth residues rom monazite sand after extraction of most of the cerium. The erium remaining was first removed by treatment of the nitrates vith bromine. Lanthanum, praseodymium, and neodymium were emoved by fractionation of the rare earth magnesium double iitrates, first from aqueous solution and then from nitric acid. Europium and gadolinium were removed by fractionation of the are earth magnesium nitrates with bismuth magnesium nitrate, he samarium material used for the atomic weight determinations eing taken from the middle series of the last fractionations. The inal purification consisted in the alternate precipitation of the amarium material as hydroxide and oxalate, and five recrystallisaions as hydrated chloride. Attempts to determine the atomic veight from the oxide–chloride ratio were abandoned, owing to he impossibility of obtaining pure oxide. The ratio hydrated hloride–anhydrous chloride was also found unsatisfactory, because of the difficulty of obtaining pure samarium chloride hexahydrate.

Finally, the anhydrous chloride–silver ratio was used, by determining the weight of silver, as nitrate, needed to precipitate the whole of the chlorine from a known weight of anhydrous samarium chloride, the end-point being determined by means of the nephelometer. A mean of eighteen determinations gave 150·43 as the atomic weight of samarium (Ag, 107·88), the extremes being 150·40 and 150·49. E. H. R.

Gadolinium. Methods of Separation of the Terbium and Ytterbium Earths. R. J. Meyer and Ulrich Müller (*Zeitsch. anorg. Chem.*, 1919, **109**, 1—30).—A number of methods of separating gadolinium from the rare earths occurring in euxenite have been examined and the efficiency of the separations compared. The alkali double sulphate method is only of use for separating a mixture which contains gadolinium into two parts, one of which contains the whole of the gadolinium. The hydrazine double sulphate method effects separation in the same way as the alkali double sulphate method, but it has the advantage of being more easily controlled. Fractional crystallisation of the bromates effects an extremely good separation of the terbium earths from the ytterbium earths, but the cerium earths cannot be separated from the terbium earths because the solubility of gadolinium bromate lies between that of samarium and neodymium bromate. Consequently, this method must be used along with another to bring about the required separation. The fractional crystallisation of the acetates effects a rapid separation of gadolinium from samarium and didymium. The great value of this method lies in the fact that it is the complement of the bromate method, and an alternation of these with the double nitrate method, which fractionates in the opposite direction, brings about a good separation. Crystallisation of the formates fractionates in the same sense as the bromates, so that a combination of the formate and acetate methods is capable of yielding pure terbium earths. Crystallisation of the double manganese nitrates, whilst very good for the separation of the cerium and yttrium earths, is found to be of very little use in separating a small amount of cerium earths from a large amount of gadolinium. Bismuth double nitrates, however, will effect this separation, and by this means a specimen of very pure gadolinium oxide was prepared. Crystallisation of the nitrates effects a fairly rapid separation of the cerium earths from gadolinium, but towards the end of the fractionation the separation becomes incomplete. The method is far inferior both in ease of manipulation and in efficiency to the acetate method. Gadolinium and terbium are easily separated by the fractional precipitation with ammonia.

The following hydrazine rare earth double sulphates have been prepared and are described: *Lanthanum hydrazine sulphate*, $La_2(SO_4)_3,(N_2H_5)_2SO_4,3H_2O$, separates in sparingly soluble, colourless crystals on warming a solution of the mixed sulphates to 75°. *Neodymium hydrazine sulphate*, $Nd_2(SO_4)_3,(N_2H_5)_2SO_4,3H_2O$, is formed in reddish-violet crystals, which separate on warming a

solution of the mixed sulphates. *Gadolinium hydrazine sulphate*, $Gd_2(SO_4)_3,(N_2H_5)_2SO_4,3H_2O$, separates in colourless, sparingly soluble crystals when a solution of the mixed sulphate is boiled for a considerable time. *Yttrium hydrazine sulphate*,

$$Y_2(SO_4)_3,(N_2H_5)_2SO_4,3H_2O,$$

is prepared by concentrating a solution of the mixed sulphates until crystallisation takes place. It is very soluble in water. *Scandium hydrazine sulphate*, $Sc_2(SO_4)_3,3(N_2H_5)_2SO_4$, is a very soluble compound which forms good crystals.

The solubility of several acetates of the rare earths has been determined in water; the following values, in grams per 100 grams of saturated solution at 25°, are given: lanthanum, 14·47; praseodymium, 21·48; neodymium, 20·76; samarium, 13·05; gadolinium, 10·37; and yttrium, 8·28. The best starting materials for the preparation of gadolinium compounds are: euxenite, samarskite, or the monazite residues, but in any case the preparation should be commenced with several kilos of material.

The following method of procedure is recommended for the purification of gadolinium compounds: (1) If the rare earth mixture contains little cerium earths and much yttrium earths the gadolinium is separated with the cerium earths in one operation by the potassium double sulphate method. (2) If the mixture contains much cerium earths the major portion of these is separated by the double nitrate method. In either case a fraction very much richer in gadolinium is obtained. This is converted into the bromates and the yttrium earths removed by fractionation. Hereby the ytterbium earths first pass into the mother liquors, then follow the erbium earths, and last of all yttrium. It is essential that the yttrium should be removed at this point, for it is scarcely possible to separate it at any of the succeeding stages. The main fraction contains samarium, gadolinium, neodymium, terbium, and europium; it is converted into acetate and fractionated, the fractionation being combined with the fractiouation of the double bismuth nitrates. The cerium earths are rapidly separated, and a brown mixture of oxides, containing gadolinium and terbium, is obtained. These two elements are rapidly separated by fractional precipitatiou with ammonia. It is possible, by the above method, to obtain pure gadolinium oxide in a few months. J. F. S.

Ammonia Derivatives of the Haloids of Bivalent Manganese and Iron. WILHELM BILTZ and GUSTAV F. HÜTTIG (*Zeitsch. anorg. Chem.*, 1919, **109**, 89—110).—The ammonia derivatives of ferrous and manganous chloride, bromide, and iodide have been investigated, some new derivatives have been prepared, and the dissociation pressure and curves of the various products have been determined for a number of temperatures. Anhydrous manganous chloride rapidly absorbs ammonia at the temperature of solid carbon dioxide and alcohol to form the hexa-ammine, $MnCl_2,6NH_3$, which is a pure white compound. At 76·5° the isothermal falls a little and then remains horizontal until the com-

position falls to that of the diamine, where the pressure falls suddenly to the value for this compound. The isothermal for the equilibrium $MnCl_2,2NH_3 \rightleftharpoons MnCl_2,NH_3 + NH_3 \rightleftharpoons MnCl_2 + 2NH_3$ has been determined at 229°, and indicates the existence of the monammine. No other ammines of manganous chloride exist in equilibrium with ammonia in the temperature and pressure range examined. The following dissociation pressures (p) and heat of dissociation (Q) have been calculated from the experimental results: hexammine, 59°, $p=218$ mm.; 63°, $p=258$ mm.; 76·5°, $p=495$ mm.; $Q=12·6K$ (mean); diammine, 181°, $p=65$ mm., $Q=18·7K$; 206°, $p=196$ mm., $Q=18·8K$; 230°, $p=407$ mm., $Q=19·1K$; monammine, 215°, $p=9·4$ mm., $Q=22·1K$; 230°, $p=28$ mm., $Q=21·75K$; 278°, $p=95$ mm., $Q=22·7K$. Manganous bromide forms similar ammines to the chloride; the following values have been calculated from the isothermals: hexammine, 107°, $p=305$ mm., $Q=14·26K$; diammine, 182°, $p=13·7$ mm., $Q=20·2K$; 215°, $p=56·4$ mm., $Q=20·4K$; 230°, $p=98·0$ mm., $Q=20·5K$. In the case of manganous iodide, the hexammine and diammine alone exist; the isothermals indicate the non-existence of a monammine; the following values are calculated: hexammine, 154°, $p=316$ mm., $Q=16·2K$; diammine, 208°, $p=11·1$ mm., $Q=21·6K$; 215°, $p=14·6$ mm., $Q=21·7K$. By similar dissociation experiments ferrous chloride is shown to form a monammine in addition to the hexammine and diammine already known. The following values for the ferrous chloride ammines are obtained: hexammine, 90°, $p=270$ mm., $Q=13·65K$; diammine, 230°, $p=121$ mm., $Q=20·3K$; 277°, $p=555$ mm., $Q=20·7K$; monammine, 214·5°, $p=5·8$ mm., $Q=22·5K$; 277°, $p=54·4$ mm., $Q=23·1K$. Ferrous chloride also forms a pure white, voluminous compound with six molecules of methylamine and a grey compound with two molecules of methylamine. Ferrous bromide absorbs ammonia rapidly at ordinary temperatures to form a white hexammine, which dissociates at elevated temperatures into a dirty white diammine, and this into a dark grey monammine. The following data are calculated from the isotherms: hexammine, 107°, $p=126$ mm., $Q=14·9K$; diammine, 215°, $p=11·5$ mm., $Q=21·9K$; 230°, $p=23·5$ mm., $Q=21·9K$; 277°, $p=126$ mm., $Q=22·3K$; monammine, 215°, $p=5·7$ mm., $Q=22·6K$; 230°, $p=9·7$ mm., $Q=22·8K$; 277°, $p=61·5$ mm., $Q=23·1K$. In the case of ferrous iodide a monammine does not exist; the following values are obtained for the other two ammines: hexammiue, 153°, $p=206$ mm., $Q=16·5K$; diammine, 215°, $p=6·1$ mm., $Q=22·5K$; 231°, $p=12·1$ mm., $Q=22·6K$; and 278°, $p=85·4$ mm., $Q=22·8K$. All the measurements and calculated values are compared with those of Ephraim (A., 1912, ii, 546; 1914, i, 17; 1913, ii, 129) and Girardet (A., 1911, ii, 43). J. F. S.

Non-rusting Iron. Hanns Fischer (*Chem. Zeit.*, 1920, **44**, 242).—A discussion on the ancient pillar of Northern India which, after 3000 years, is quite free from rust. A satisfactory explanation of the phenomenon is not yet forthcoming. E. H. R.

Cobaltammines. NIL RATAN DHAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 576—579. Compare A., 1913, ii, 319; 1914, ii, 57).—The preparation of cobaltammines is guided by the law of mass action, and thus depends on the concentration of the reacting substances. A nitro-group in a compound may be replaced by an amino-group by warming the compound with a mixture of ammonium hydroxide and an ammonium salt, whilst the reverse change is brought about when the salt is warmed with a nitrite solution.

The hydrolysis of purpureo-cobalt chloride to give aquopentamminecobalt chloride,

$$\left[Co\begin{matrix}(NH_3)_5\\ Cl\end{matrix}\right]Cl_2 + H_2O \rightleftharpoons \left[Co\begin{matrix}(NH_3)_5\\ H_2O\end{matrix}\right]Cl,$$

is catalytically accelerated by the presence of hydroxyl ions.

The hydroxides of the cobaltammines may be prepared in solution by treating the corresponding haloid with moist silver oxide, but purpureo-cobalt chloride under these conditions gives aquepentamminecobalt hydroxide. W. G.

The Constitution of Two Cobaltammines. PAUL JOB (*Compt. rend.*, 1920, **170**, 731—734).—Titration of roseo-cobaltic sulphate by barium hydroxide, the action being followed by electrical conductivity measurements, shows that the action takes place in two stages. The curve has two singular points, the first corresponding with the precipitation of one-third of the sulphuric acid and the second with its complete precipitation. These results support Werner's view as to the constitution of the roseo-cobalt salts, the changes being given by

$$\left[Co\begin{matrix}(NH_3)_5\\ H_2O\end{matrix}\right]_2(SO_4)_3 + Ba(OH)_2 = \left[Co\begin{matrix}(NH_3)_5\\ (OH)\end{matrix}\right]_2(SO_4)_2 + BaSO_4 + 2H_2O$$

$$\left[Co\begin{matrix}(NH_3)_5\\ (OH)\end{matrix}\right]_2(SO_4)_2 + 2Ba(OH)_2 = \left[Co\begin{matrix}(NH_3)_5\\ (OH)\end{matrix}\right]_2(OH)_4 + 2BaSO_4.$$

The author has isolated the intermediate *compound*,

$$Co(NH_3)_5(OH)SO_4,2H_2O,$$

in a crystalline form.

In the same way diroseo-cobalt sulphate when titrated with barium hydroxide gives a singular point when two-thirds of the sulphuric acid is precipitated, and another when the whole of it is precipitated. W. G.

Green Double Salts of Chromium Chlorides. NILS LARSSON (*Zeitsch. anorg. Chem.*, 1920, **110**, 153—165).—A number of new double salts formed by monochloroaquochromium chloride,

$$[CrCl(H_2O)_5]Cl_2,$$

and dichloroaquochromium chloride, $[CrCl_2(H_2O)_4]Cl$, with chlorides and sulphates of different bases have been prepared. The double salts correspond in colour with the simple chromium compounds, the dichloro-compounds being light green and the monochloro-compounds light bluish-green. The compounds of the former class

are more hygroscopic, and, in general, less readily soluble than those of the latter. In all the compounds described containing the sulphate radicle, the whole of this radicle is precipitated by barium nitrate, and is therefore outside the complex chromium radicle. The following compounds were prepared.

Double Salts with Sulphates.—(1) Dichlorochromi-compounds: $[CrCl_2(H_2O)_4]Cl,2(NH_4)_2SO_4,2H_2O$; $[CrCl_2(H_2O)_4]_2SO_4,3(NH_4)_2SO_4$; $[CrCl_2(H_2O)_4]_2SO_4,(NH_4)_6H_2(SO_4)_4$; tetramethylammonium compound, $[CrCl_2(H_2O)_4]SO_4,(NMe_4)_2SO_4,3H_2O$; methylammonium compounds, $[CrCl_2(H_2O)_4]_2SO_4,3(NH_3Me)_2SO_4$;

$$[CrCl_2(H_2O)_4]_2SO_4,(NH_3Me)_6H_2(SO_4)_4;$$

tetraethylammonium compound,

$$[CrCl_2(H_2O)_4]_2SO_4,(NEt_4)_2SO_4,10H_2O;$$

ethylammonium compound, $[CrCl_2(H_2O)_4]_2SO_4,(NH_3Et)_2SO_4,6H_2O$; guanidine compounds, $[CrCl_2(H_2O)_4]_2SO_4,3(CN_3H_6)_2SO_4$;

$$[CrCl_2(H_2O)_4]_2SO_4,(CN_3H_6)_6H_2(SO_4)_4;$$

pyridine compound, $[CrCl_2(H_2O)_4]_2SO_4,(C_5NH_6)_2SO_4,4H_2O$.

(2) Monochlorochromium compounds: ammonium compounds, $[CrCl(H_2O)_5]Cl_2,(NH_4)_2SO_4,H_2O$, $[CrCl(H_2O)_5]SO_4,(NH_4)_2SO_4$; $[CrCl(H_2O)_5]SO_4,(NH_4)HSO_4$; methylammonium compound, $[CrCl(H_2O)_5]SO_4,(NH_3Me)_2SO_4$; dimethylammonium compound, $[CrCl(H_2O)_5]SO_4,(NH_2Me_2)_2SO_4$; tetramethylammonium compound, $2[CrCl(H_2O)_5]SO_4,(NMe_4)_2SO_4$; ethylammonium compound, $2[CrCl(H_2O)_5]SO_4,(NH_3Et)_2SO_4,4H_2O$; hydroxylamine compounds, $2[CrCl(H_2O)_5]Cl(SO_4)_{\frac{1}{2}},(NH_4O)_2SO_4,2H_2O$, and

$$[CrCl(H_2O)_5]SO_4,NH_2\cdot OH,H_2SO_4;$$

pyridine compound, $2[CrCl(H_2O)_5]SO_4,(C_5H_6N)_2SO_4$; strychnine compound, $2[CrCl(H_2O)_5]SO_4,(C_{21}H_{22}N_2O_2)_2SO_4$.

Double Salts with Chlorides.—Rubidium compound,

$$[CrCl_2(H_2O)_4]Cl,2RbCl,$$

stable in air, heated at 85°, loses three molecular proportions of water and changes into Neuman's salt, $[CrCl_5(H_2O)]Rb_2$; ammonium compound, $[CrCl(H_2O)_5]Cl_2,NH_4Cl,H_2O$; rubidium compound, $[CrCl(H_2O)_5]Cl_2,RbCl$; cæsium compound, $[CrCl(H_2O)_5]Cl_2,CsCl$. No potassium salt could be prepared, but a very hygroscopic lithium salt was obtained. E. H. R.

Chromi-aquo-triammines. FR. FROWEIN (*Zeitsch. anorg. Chem.*, 1920, **110**, 107—124).—Conductivity measurements have been made on the three compounds, dichloromonaquotriammin-chromichloride, $[Cr(NH_3)_3Cl_2,H_2O]Cl$; monochlorodiaquotriammin-chromichloride, $[Cr(NH_3)_3Cl(H_2O)_2]Cl_2$; and triaquotriammin-chromichloride, $[Cr(NH_3)_3(H_2O)_3]Cl_3$. Three isomerides of the monoaquo-compound have been described by Seemann (*Inaug. Diss.*, 1910, p. 27), but, of these, only the chloride I was examined. The compounds were prepared by Seemann's methods with slight modifications. The monaquo-compound gradually passes over in solution into the diaquo-, and this, in turn, into the triaquo-compound, and on this account it was necessary to make the conductivity measurements on the freshly prepared solutions. The

changes can be followed by the change of colour of the solution, that of the monoaquo-compound being blue, that of the diaquo reddish-violet, and that of the triaquo red. These changes are more rapid the more dilute the solutions. The conductivity of the monoaquo-compound is lowest, that of the triaquo-compound highest, so that the change is accompanied by a gradual increase in conductivity of the solution. No direct transformation of the mono- into the tri-aquo-compound occurs, but the diaquo-compound is always the first hydration product of the monoaquo. It is concluded from the measurements that the compounds contain no water outside the inner sphere, that is, they are purely co-ordinated compounds. The solution of the triaquo-compound undergoes slow decomposition, the conductivity curve first showing a maximum, followed by a minimum. Deposition of chromium hydroxide eventually takes place, but intermediate complex compounds are probably first formed. E. H. R.

Recovery of Ammonium Molybdate from Residues, etc., obtained in Estimating Phosphoric Acid by Lorenz's Method. H. NEUBAUER and E. WOLFERTS (*Zeitsch. anal. Chem.*, 1919, **58**, 445—448).—The filtrates, precipitates, etc., obtained in Lorenz's method (A., 1901, ii, 278) are partially neutralised with ammonia, and the molybdic acid is precipitated at 80° by the addition of an excess of sodium phosphate; the yellow precipitate is collected, dissolved in ammonia, the phosphoric acid precipitated by the addition of magnesium nitrate, the precipitate removed, and the filtrate concentrated. Ammonium molybdate crystallises out, and is purified by recrystallisation, first from very dilute ammonia solution, and then from water. W. P. S.

The Uranyl Radicle as a Chromophore. ARNÖ MÜLLER (*Zeitsch. anorg. Chem.*, 1919, **109**, 235—274).—The colour of a large number of uranyl salts is considered; the colour is, in general, yellow, but the presence of hydroxyl or keto-groups, particularly in the α- or ortho-positions, displaces the colour strongly towards the red. The benzene nucleus also acts strongly in displacing the colour towards the red end of the spectrum, particularly when the uranyl group is directly connected with phenolic oxygen. The author has tabulated the formulæ, crystal system, melting point, solubility in water, alcohol, and ether, and colour of fifty-five monocarboxylic, dicarboxylic, hydroxy-carboxylic, phenolcarboxylic, and polycarboxylic acid salts of the uranyl group. The method of preparation and the properties of fifty-two uranyl salts of aromatic and aliphatic acids of various types are described. J. F. S.

Some Compounds of Zirconium and the Hydrolysis of its Salts. ED. CHAUVENET (*Ann. Chim.*, 1920, [ix], **13**, 59—86).—A résumé of work already published (compare A., 1914, i, 321; 1917, ii, 264, 321, 322, 374, 416; 1918, ii, 234, 269, 321). W. G.

Alloys of Gold and Silicon. CLARA DI CAPUA (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 111—114).—Warren (A., 1893, ii, 474) and Vigouroux (A., 1896, ii, 600) have shown that gold forms an alloy with silicon. The author has studied the diagram of state of the system gold, of 0·999 purity and silicon containing 4—5% of impurity, mostly iron, being used. Fusion and cooling of the mixtures were carried out in a rapid current of hydrogen. Owing to the low thermal conductivity of silicon, the duration of the arrests of the cooling was very irregular, and yielded no information. The cooling results show that gold and silicon are miscible in all proportions in the liquid condition, that they form no compounds, and that they are non-miscible in the solid state, at any rate within the limits of the experimental accuracy attained. The eutectic alloy melts at 370°. With the alloy containing 85% of silicon, no retardation corresponding with the solidification of the eutectic is observable, but microscopic examination reveals crystals of gold scattered throughout the mass; the formation of mixed crystals at this concentration is therefore excluded. Almost all the alloys rich in silicon exhibit at the surface a golden-yellow globule, which is sharply detached from the greyish-blue, metallic block, and contains a greater proportion of gold than the mixture from which it is formed. A similar globule has been observed with silicon–silver alloys (compare Arrivaut, A., 1908, ii, 1035) and with silicon–aluminium alloys (compare Fraenkel, A., 1908, ii, 592), and its formation is certainly due to the fact that silicon solidifies with increase of volume. Hence, during the solidification, the part which solidifies last, namely, the eutectic, is forced upwards and forms the globule.

The melting point of gold is lowered by about 800° by 6—7% of silicon.

Microscopic examination of the alloys fully confirms the results of the thermal analysis. T. H. P.

Ammonium Pentahalogenoruthenates. A. GUTBIER (*Zeitsch. anorg. Chem.*, 1919, **109**, 187—212).—Polemical. A criticism of statements as to ruthenium and its double chlorides in a paper by Mylius and Mazzucchelli (A., 1915, ii, 491), in which it is shown that the method of preparation of ammonium pentachlororuthenate suggested by these authors is not capable of giving this compound. [See also Guthier and Trenkner, A., 1905, ii, 463.]

J. F. S.

Mineralogical Chemistry.

Bismutoplagionite, a New Mineral. EARL V. SHANNON (*Amer. J. Sci.*, 1920, [iv], **49**, 166—168).—A lead-grey, indistinctly fibrous mineral associated with pyrites, quartz, etc., was sent from Wickes, Montana. The streak is dark brownish-grey; D 5·35, H 2·8. The mineral is completely soluble in hot concentrated hydrochloric acid, whilst the pyrites is only slightly attacked. In the analysis (I), the sulphur was estimated by difference, the iron being assumed to represent pyrites; the insoluble portion also consisted mainly of pyrites. Deducting these impurities, the recalculated composition II agrees with the formula $5PbS,4Bi_2S_3$, in which a small amount of the bismuth is replaced by antimony.

	PbS.	FeS_2.	Sb_2S_3.	Bi_2S_3.	Insoluble.	As_2S_3,CuS,Ag_2S.	Total.
I.	30·21	1·25	3·37	45·62	18·88	traces	99·33
II.	38·13	—	4·26	57·61	—	—	100·00

The ratio $PbS:R_2S_3$ being the same as in plagionite,

$$(5PbS,4Sb_2S_3),$$

the mineral is placed in the plagionite group, together with liveingite ($5PbS,4As_2S_3$), rather than with galenobismutite (PbS,Bi_2S_3). L. J. S.

Hæmatite and Rutile formed by the Action of Chlorine at High Temperatures. H. E. MERWIN and J. C. HOSTETTER (*Amer. Min.*, 1919, **4**, 126—127).—In the course of experiments on the removal of iron from clay pots by leading chlorine into the covered pots, heated in a gas-fired furnace at 1000—1100°, when they were removed from the furnace directly after the chlorine treatment, a deposit of hæmatite crystals was found on the outer, upper portion of the pot where chlorine and vaporised ferric chloride had come into contact with the products of combustion of the furnace. The crystals were in the form of rhombohedra with perfect faces. On the inside of one of the pots were found crystals of rutile in the form of very thin, twinned plates. The formation of crystals of hæmatite and rutile from vapours containing ferric chloride or titanium chloride has been previously recorded.

E. H. R.

Calcite from New York State. H. F. GARDNER (*Amer. Min.*, 1920, **5**, 3—5).—Enormous crystals (180 kilos.) of calcite of a dull lavender or violet colour were obtained from a cave in a limestone quarry at Sterlingbush, Lewis Co., N.Y. These have been grouped as a cave in the New York State Museum at Albany, and by transmitted lamp light show a deep rose-red to light pink colour. They

contain Fe 0·08, Mn 0·12, Mg 0·09, corresponding with $FeCO_3$ 0·17, $MnCO_3$ 0·25, $MgCO_3$ 0·32. Neodymium, to which the colour is attributed (A., 1917, ii, 209), is present in amounts too small for analytical recognition. L. J. S.

Latent Heat of Fusion of Cristobalite. E. W. WASHBURN (*J. Amer. Ceram. Soc.*, 1919, **2**, 1007—1008).—The author assumes that, in binary systems containing some alumina and a large proportion of silica, the solute exists in the form of molecules having simple molecular weights, and calculates the latent heat of fusion of cristobalite by means of the law regulating the lowering of the fusion point of dilute solutions, using the formula $L=RT^2/\Delta t \, . \, x$, where L = the latent heat of fusion, R = the gas constant (2 cal.), T = the absolute melting point of cristobalite (1983° abs.) (1610° is the melting point of the eutectic for binary mixtures of alumina and silica containing 87 per cent. of silica and 13 per cent. of alumina), t = the lowering of the freezing point (1710—1610°), and x = the molar fraction of the solute.

Assuming the solute is sillimanite, Al_2SiO_5, L = 6950 cal. per mol.; on the less probable assumption that the solute is alumina, Al_2O_3, L = 6360 cal. per mol. Giving greater weight to the former assumption, the author suggests that the latent heat of fusion of cristobalite is 6800 cal. per mol. If the molecules of the solute are associated, and so ought to be represented by layer integers in the formulæ, the heat of fusion obtained by calculation in this manner is too large. A. B. S.

Fusion and Transition Phenomena of Spodumene. F. MEISSNER (*Zeitsch. anorg. Chem.*, 1920, **110**, 187—195).—The transition from α- to β-spodumene proceeds rapidly when the mineral is heated above 1000°. Experiments were made with the object of determining whether the transition is reversible. The spodumene was first heated for one and a-half hours at 900° to start the change into the β-form, and then samples, of varying degrees of fineness, were heated for varying periods at temperatures from 800° to 900°, the course of change being followed by density determinations. In every case the change into the β-form proceeded, no evidence of reversibility being obtained. The transition could be detected by optical means, in the case of thin cleavage plates, after heating for three hours at 720°, that is, 150° lower than the minimum temperature at which a change of density can be detected. In agreement with the work of Ballo and Dittler (A., 1912, ii, 758), no evidence of reversibility could be detected by thermal methods. The so-called γ-form of spodumene, which crystallises from the molten material, has been examined and compared with the β-form. In all probability the two forms are identical. The refractive indices are not appreciably different, and the difference between the melting points observed by the above authors (1380° for the β-form and 1290° for the γ-form) is probably due to the low fusion and crystallisation velocity of the substance. E. H. R.

Echellite, A New Mineral. N. L. Bowen (*Amer. Min.*, 1920, **5**, 1—3).—This occurs as small, white, spheroidal masses of radiating fibres in a basic igneous rock at the Sextant portage, Abitibi river, northern Ontario. The optical characters point to orthorhombic symmetry; $\alpha=1{\cdot}530$, $\beta=1{\cdot}533$, $\gamma=1{\cdot}545$; positive. It is easily decomposed by hydrochloric acid. Analysis:

SiO_2.	Al_2O_3.	CaO.	BaO.	Na_2O.	K_2O.	H_2O.	Total.
34·5	40·0	7·2	nil	4·1	trace	14·4	100·2

gives the formula $(Ca,Na_2)O,2Al_2O_3,3SiO_2,4H_2O$. The name *echellite* (from French, *échelle*, ladder) alludes to the stepped ratios, 1, 2, 3, 4, in this formula. The ratio $CaO:Na_2O=2:1$. The mineral shows certain resemblances to the zeolites, but in the latter the ratio $Al_2O_3:(Ca,Na_2)O$ is nearly always 1:1. The formula is written in the form $(Ca,Na_2)Al(OH)_2Al_2(SiO_4)_3,3H_2O$ to show a relation to zoisite. L. J. S.

Zebedassite, a New Hydrated Silicate of Aluminium and Magnesium from Zebedassi in the Pavian Apennines. Amalia Brusoni (*Rend. R. Ist. Lombardo Sci. Lett.*, 1917, [ii], **50**, 646—650; *Riv. Min. Crist. Ital.*, 1918, **50**, 74—79).—The mineral fills fissures in an altered rock found as loose blocks on a hill of serpentine at Zebedassi, near Volpedo. The rock (partial anal. I) has probably been derived from granite or gneiss. The new mineral forms white, fibrous aggregates with silky lustre. The fibres have straight optical extinction, and are probably orthorhombic; $n=1{\cdot}51$—$1{\cdot}53$, D 2·194, H 2. The mineral is easily soluble in acids with separation of gelatinous silica. Some water is lost over sulphuric acid, and between 105° and about 200° the loss is 2·40%. Analysis II of material dried at 105°:

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	H_2O (over 105°).	Total.
I.	47·06	9·80	8·09	0·82	23·58	9·01	—
II.	50·27	12·90	—	—	26·98	10·49	100·64

In the earlier publication the formula is given as

$$9H_2O,2Al_2O_3,11MgO,13SiO_2,$$

but in the later it is written more simply as

$$4H_2O.Al_2O_3,5MgO,6SiO_2$$

or $H_8Al_2Mg_5(SiO_4)_6$. The mineral is near neolite. L. J. S.

Analytical Chemistry.

Analytical Weighing. HORACE L. WELLS (*J. Amer. Chem. Soc.*, 1920, **42**, 411—419).—The author advocates the use of the short swing method of weighing in place of the more tedious long swing method so often advocated in text-books. E. H. R.

A Nephelometer. CHARLES CHÉNEVEAU and RENÉ AUDUBERT (*Compt. rend.*, 1920, **170**, 728—731).—The construction of the nephelometer is based on the formula $I/I_0 = 1 - e^{-B/M^\beta}$, where I and I_0 are the intensity of the transmitted and incident light respectively and M the total mass of the particles in suspension in the medium. The absorption of the medium is compensated by a prism of very slight angle, of neutral tinted glass. It is shown that the displacement, x, of this prism for the compensation is a linear function of M, and consequently the value of M may be read off directly on a scale. [See, further, *J. Soc. Chem. Ind.*, 1920, 350A.] W. G.

Machine for Washing Precipitates. ERIC SINKINSON (*Analyst*, 1920, **45**, 94—97).—The funnel containing the filter and precipitate to be washed is supported in a ring at one end of a counterpoised rocking arm; the latter is connected with a commutator to reverse a motor actuating the valve on the water supply. When the motor is started, the valve is opened and water is admitted through a rotating jet on to the precipitate. As soon as a certain weight of water has collected in the funnel, the rocking arm is depressed, the motor is reversed, and the valve closed. As soon as a sufficient quantity of water has passed from the funnel, the rocking arm rises, the motor is thus again reversed, and water admitted to the funnel, and so on. W. P. S.

New, Simple and Rapid Process for Collecting and Characterising the Films Produced by Metalloids and Metals capable of being Volatilised by Heat. AD. BRALY (*Compt. rend.*, 1920, **170**, 661—663).—A simple portable apparatus is described for use in the field by prospectors in the examination of minerals. It consists essentially of two plates of mica, suitably mounted, on one of which the mineral is heated in the blowpipe flame, the second being so adjusted as to condense and collect the resulting volatile vapours. To the film thus obtained the usual tests, for characterising the metals present, may be applied. By suitably regulating the flame temperature it is possible to obtain successive films from the different metals or metalloids present in the mineral. W. G.

The Titration of Mixed Acids by Conductivity Methods. I. M. KOLTHOFF (*Rec. trav. chim.*, 1920, **39**, 280—302).—For the most part, the results confirm the work of Meerburg (compare A.,

1919, ii, 518). It is not possible to estimate lactic acid in gastric juice by the conductivity method, although the total acidity of the juice may be readily determined by this method.

The method is suitable for estimating, with a very fair degree of accuracy, either small amounts of weak acids, such as acetic acid, mixed with larger amounts of strong acids, such as hydrochloric acid, or vice versa, and may be applied, therefore, to the estimation of mineral acids in vinegar. Weak bases may similarly be estimated in the presence of strong bases by the conductivity titration method. W. G.

A Simple, Rapid Method for the Estimation of Halogen in Organic Substances. W. A. VAN WINKLE and G. McP. SMITH (*J. Amer. Chem. Soc.*, 1920, **42**, 333—347).—A simple and accurate combustion method has been developed for the estimation of chlorine, bromine, or iodine in readily volatile organic compounds. The weighed material is volatilised with air from a specially designed sample holder, and is passed through a quartz tube heated for a length of about 25 cm. at 900—1000°. The products of combustion pass to an absorption apparatus containing an absorbing solution, prepared by mixing 25 c.c. of 5*N*-sodium hydroxide solution with 10 c.c. of 2*N*-sodium sulphite solution. The sulphite serves to reduce any oxy-halogen salts formed. The time taken for the combustion is from one to two hours. The excess of sulphite in the absorbing solution is then oxidised with potassium permanganate, and the halogen estimated by the Volhard process. The method was used for the analysis of ethyl bromide, ethyl iodide, ethylene chloride, bromobenzene, allyl bromide, chloroform, chloropicrin, and a number of other compounds, and gave results equal or superior to those given by the Carius method. With a slight modification of the apparatus, equally good results were obtained for less volatile substances, such as hexachlorobenzene, *m*-chloronitrobenzene, and *p*-bromoaniline.
E. H. R.

Detection of Chloride in the Presence of Bromide. CARL FAURHOLT (*K. Danske Vidensk. Medd. Math. Phys.*, 1919, **2**, No. 9, 1—16; from *Chem. Zentr.*, 1920, ii, 424).—Hager's method, which depends on the separation of the silver haloids from one another by taking advantage of their differing solubilities in ammonia and ammonium sesquicarbonate solution, is modified by the substitution of very dilute ammonia to which a little silver nitrate is added, in order to depress the solnbility of silver bromide without sensibly altering that of silver chloride. Potassium nitrate is also added to prevent the possibility of the formation of colloidal solutions (0·25 mol. NH_3 + 0·01 mol. $AgNO_3$ + 0·25 mol. KNO_3 or 0·50 mol. NH_3 + 0·05 mol. $AgNO_3$ + 0·25 mol. KNO_3 per litre).
H. W.

Chlorides in Water Analysis. E. MALMEJAC (*J. Pharm. Chim.*, 1920, [vii], **21**, 263—268).—Results of analyses of various waters

are recorded, and attention is directed to the fact that the quantity of chlorine present affords a useful indication of the presence or absence of animal-polluting substances, especially when the normal chlorine content of the water is known. W. P. S.

Estimation of Chlorides in Whole Blood. J. HAROLD AUSTIN and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1920, **41**, 345—348).—The protein is precipitated from the blood by picric acid, or by a mixture of picric and nitric acids. The protein-free filtrate is then treated with silver nitrate, a quantitative precipitation of the total chlorides being obtained. The final titration may be carried out by the Van Slyke-Donleavy process (A., 1919, ii, 239). J. C. D.

The Estimation and Kinetics of Hypoiodous Acid in Acid Solution. VICTOR COFMAN (*Bull. Soc. chim.*, 1920, [iv], **27**, 234—239).—Hypoiodous acid reacts almost instantaneously with phenolic compounds, giving stable iodo-compounds (compare T., 1919, **115**, 1040), and on this is based the method for estimating this acid in the presence of free iodine or other iodine compounds. To a known, suitable volume of the liquid under examination, potassium iodide is added, and, after acidifying, if necessary, the free iodine is titrated with standard thiosulphate. This operation is then repeated, but an excess of phenol is added before the potassium iodide. The difference in the amount of iodine found by these two titrations is a measure of the amount of hypoiodous acid present. An examination of the reversible action $2I_2 + HIO_3 + 2H_2O \rightleftharpoons 5HIO$ shows that the velocity of formation of hypoiodous acid is that of a bimolecular reaction. Similarly, measurements of the velocity of decomposition of the acid show that this change is also bimolecular. W. G.

Gravimetric Analysis. XII. Estimation of Sulphuric Acid. II. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1920, **33**, 59—60).—Investigation of the precipitation of sulphuric acid as barium sulphate showed that when the acidity of the solution was reduced to $N/100$ by the addition of potassium carbonate or ammonia, the solution then boiled, treated with barium chloride solution, and the precipitate collected after eighteen hours, the weight of the precipitate, dried at 130° (about 0·3 gram), required to be multiplied by 1·0045 to obtain the correct weight. If the precipitate was ignited before being weighed, the factor was 1·0099. It was proved that the barium sulphate dried at 130° lost a small quantity of sulphuric acid when ignited. If sodium carbonate was used for the neutralisation of the sulphuric acid, the results obtained were not concordant. W. P. S.

The Kjeldahl Method for the Estimation of Nitrogen. I. K. PHELPS and H. W. DAUDT (*J. Assoc. Off. Agric. Chem.*, 1919, **3**, 218—220).—By using 0·7 gram of mercuric oxide, 10 grams of potassium sulphate and 25 c.c. of sulphuric acid, with

from 0·2 to 0·4 gram of substance, it was found that the Kjeldahl method was trustworthy for the estimation of nitrogen in the following compounds: glucosamine hydrochloride, isatin, atropine, cocaine, nicotinic acid, alkaloids, including caffeine, quinoxaline hydrochloride, 2-methyl-4-quinazolone, and 3-phenyl-2-methyl-4-quinazolone. The hydrolysis required 2·5 hours. W. P. S.

Use of Potassium Permanganate in Estimating Nitrogen by the Kjeldahl Method. WILLIAM FREAR, WALTER THOMAS, and H. D. EDMISTON (*J. Assoc. Off. Agric. Chem.*, 1919, **3**, 220—224).—In estimating nitrogen in a number of different fertilisers, there was a considerable loss of nitrogen when permanganate was added at the end of the acid digestion period; the extent of the loss depended on the amount of permanganate added, and more particularly on the time at which the addition was made. If the addition was delayed for two minutes after the burner had been removed, there was no loss of nitrogen.

W. P. S.

A Modification of the Apparatus for the Estimation of Arginine Nitrogen by Van Slyke's Method. GEORGE E. HOLM (*J. Amer. Chem. Soc.*, 1920, **42**, 611—612).—A modified apparatus for the Van Slyke estimation of arginine consists of a Kjeldahl flask fitted with a cork, which carries a tap funnel for the addition of water at the end of the potassium hydroxide digestion, and the elongated, water-jacketed tube of a Kjeldahl still-head. This arrangement obviates loss of material by bumping, or of ammonia in the transference from one vessel to another, in the ordinary procedure. J. K.

Distillation of Ammonia. B. S. DAVISSON (*J. Ind. Eng. Chem.*, 1920, **12**, 176—177).—For the distillation of ammonia in the estimation of nitric nitrogen (A., 1919, ii, 242), the most trustworthy results are obtained by the use of a condenser of block tin and the scrubber previously described (A., 1919, ii, 296). In using this apparatus with the ordinary Kjeldahl process, the following method of distillation removes the last traces of ammonia from the condenser without unduly increasing the volume of liquid in the receiving flask, which leads to hydrolysis of the indicator salt. The solution is slowly distilled for twenty minutes, so as to collect about 80 c.c. of distillate, the condenser then drained, and the distillation continued for another fifteen minutes. The receiver is then covered to prevent absorption of carbon dioxide, and the distillate cooled and titrated. C. A. M.

Volumetric Estimation of Ammonia in Blood. P. GERARD (*Compt. rend. Soc. Biol.*, 1919, 1186; from *J. Pharm. Chim.*, 1920, [vii], **21**, 236—237).—Ten c.c. of the blood are collected in potassium oxalate solution in a test-tube 22 cm. in depth, 10 c.c. of 29% sodium carbonate solution and 2 c.c. of octyl alcohol are added (the alcohol prevents excessive frothing), and air is aspirated

through the mixture at the rate of 3 litres a minute for about seventy minutes. The test-tube is connected with an absorption vessel containing a definite quantity of $N/100$-sulphuric acid, which absorbs the ammonia, and the excess of acid is titrated subsequently with sodium hydroxide solution, using methyl-orange as indicator. W. P. S.

Estimation of the Nitro-group in Aromatic Organic Compounds. T. Callan, J. A. Russell Henderson, and N. Strafford (*J. Soc. Chem. Ind.*, 1920, **39**, 86—88T).—Although the nitro-group in many organic compounds may be estimated by reduction with titanium trichloride solution, the excess of the latter being titrated subsequently, in the case of *a*-nitronaphthalene, *o*-nitroanisole, nitrotolyl methyl ether, and similarly constituted compounds, the results obtained are much too low, owing to the formation of chlorinated amines. If titanous sulphate is used in place of titanium trichloride, chlorination does not occur, and the results obtained are trustworthy. Methods involving the use of stannous chloride also possess the disadvantage that, in certain cases, chlorinated compounds are formed. A method depending on the reduction of the nitro-group with zinc and hydrochloric acid, and titration of the amine with sodium nitrite solution, yielded trustworthy results with such compounds as chloronitrobenzene-*o*-sulphonic acid, nitroanisole, *p*-nitrotoluenesulphonic acid, etc. W. P. S.

The Acidimetric Estimation of Boric Acid. J. A. M. van Liempt (*Rec. trav. chim.*, 1920, **39**, 358—370).—Boric acid may be estimated electrometrically by measuring the hydrogen-ion concentration of the solution after successive additions of standard alkali, providing a suitable excess of either mannitol, glycerol, or lævulose is previously added. The volume of alkali added is plotted against the values of p_H, and the curve shows a very marked inflexion at the neutralisation point if sufficient of the polyhydric alcohol has been added. W. G.

Estimation of Available Oxygen in Sodium Perborate and in Perborate Soap Powders. H. Trickett (*Analyst*, 1920. **45**, 88—91).—Titration of the perborate with permanganate solution is not very trustworthy; the best results are obtained by adding a slight excess of the perborate solution to a definite quantity of $N/10$-permanganate solution acidified with sulphuric acid, and then titrating the excess with permanganate solution. The temperature of the solution should be about 15°, and the acidity 5% of sulphuric acid, calculated on the total volume. The gasometric method for the estimation of perborate by means of permanganate is untrustworthy. A gasometric method depending on the decomposition of the perborate with hypochlorite is described. The perborate solution is treated in a nitrometer with sodium hypochlorite solution, and the volume of oxygen measured after the mixture has been shaken for five minutes. This method

may be applied directly to perborate soap powders, and the results obtained agree with those yielded by the usual iodometric method.
W. P. S.

Estimation of Carbon. L. LESCŒUR (*J. Pharm. Chim.*, 1920, [vii], **21**, 257—263).—The organic substance is mixed in a covered silver crucible with a mixture consisting of equal weights of sodium nitrate and potassium nitrate, sodium hydroxide solution (free from carbonate) is added, the whole is dried, and then fused. After cooling, the mass is dissolved in water, ammonium chloride and calcium chloride are added, and the resulting calcium carbonate is collected, washed, and titrated with $N/1$-hydrochloric acid, using methyl-orange as indicator. [See, further, *J. Soc. Chem. Ind.*, 1920, May.] W. P. S.

Rapid Method for the Estimation of Carbon in Organic Mixtures, particularly in Urine. L. LESCŒUR and O. DUTRIEUX (*Compt. rend. Soc. Biol.*, 1919, **82**, 1417—1418; from *Chem. Zentr.*, 1920, ii, 427).—The specimen, containing 100—200 mg. of carbon, is heated in a suitable vessel, preferably a silver crucible provided with a lid and exit tube, with an excess of sodium hydroxide (about 50 c.c. of a N-solution), and 10 grams of a mixture of equal amounts of potassium and sodium nitrates until vapours are no longer evolved, and finally to redness for a short time. The product is dissolved in hot water, and the alkali carbonate formed is estimated titrimetrically. H. W.

Combustion by the Sulphochromic Mixture of Organic Compounds containing Chlorine. J. GUYOT and L. J. SIMON (*Compt. rend.*, 1920, **170**, 734—736).—The method of oxidation of methyl esters by a mixture of sulphuric and chromic acids (compare this vol., i, 284) has been extended to chloro-compounds with success. It is necessary to interpose between the reaction vessel and the gas burette, where the carbon dioxide is measured. an amalgamated spiral of copper to retain the chlorine. In addition, in some cases there is a tendency to form carbonyl chloride, but this can be overcome by using an excess of chromic acid.

Theoretical results were obtained with methyl chlorosulphonate and chloroformate, but in the case of the ethyl esters, the ethyl group did not readily undergo oxidation. It is of interest to note that, whereas acetic acid did not undergo oxidation by this method (*loc. cit.*), its chloro-derivatives are completely oxidised. This difference is confirmed by a comparison of the behaviour of hydrocarbons and their chloro-derivatives towards this oxidising agent. W. G.

Estimation of Mineral Constituents in Organic Substances, especially those containing Phosphorus. J. GROSSFELD (*Chem. Zeit.*, 1920, **44**, 285—286).—The addition of magnesium acetate solution is recommended; after the mixture

has been dried, it is readily ignited, and the ash is free from unburnt carbon. Allowance must be made for the amount of magnesium oxide added as acetate. W. P. S.

Explosion during the Separation of Potassium by the Perchlorate Method. A. F. JOSEPH and F. J. MARTIN (*J. Soc. Chem. Ind.*, 1920, **39**, 94T).—To estimate sodium in a plant ash, the potassium was separated by precipitation as perchlorate, the filtrate and alcoholic washings (containing the sodium and excess of perchloric acid) were evaporated, and the sodium estimated as sulphate. On one occasion, when the alcoholic solution had been evaporated to a volume of a few c.c., violent explosion occurred. Possibly, some non-volatile substance derived from the alcohol reacted with the concentrated perchloric acid. W. P. S.

Estimation of Magnesium in Blood. W. DENIS (*J. Biol. Chem.*, 1920, **41**, 363—365).—The citrated plasma, serum, or whole blood is precipitated by three volumes of 6·5% trichloroacetic acid solution. The filtrate is used for the estimation of calcium, which is precipitated as oxalate by Lyman's method (A., 1917, ii, 271). The filtrate from the calcium is evaporated to dryness in a platinum dish with a small volume of 10% sulphuric acid and ignited over a free flame for two or three minutes. The cooled residue is dissolved in a small volume of distilled water, and the magnesium is precipitated as ammonium magnesium phosphate. An indirect estimation of the magnesium in this precipitate is then made by an estimation of the phosphate present by the nephelometric method with the strychnine molybdate reagent. J. C. D.

Estimation of Mercury by Glückmann's Method and Modifications of the same. ARTHUR ABELMANN (*Zeitsch. anal. Chem.*, 1919, **58**, 443—445).—The method (compare Peters, A., 1900, ii, 576) is liable to give untrustworthy results, owing to the solubility of mercury oxalate and the formation of basic salts, but this may be prevented by the addition of 2—3 c.c. of 5*N*-nitric acid to the mercury solution, using a large excess of oxalic acid for the precipitation, and introducing 50 c.c. of saturated potassium nitrate solution before the excess of oxalic acid is titrated with permanganate. W. P. S.

Estimation of Mercury in Organic Compounds. A. WÖBER (*Zeitsch. angew. Chem.*, 1920, **33**, 63—64).—The organic matter is destroyed by heating 0·5 gram of the substance with 5 c.c. of sulphuric acid in a flask fitted with a tapped funnel and a delivery tube connected with a Peligot tube cooled externally with water; 1 c.c. of concentrated hydrogen peroxide solution is added, drop by drop, through the funnel, and the heating is continued until sulphur trioxide fumes appear in the Peligot tube and a clear solution is obtained in the flask. The contents of the latter are then cooled, diluted, 1 gram of sodium chloride is added, the mix-

ture neutralised with sodium hydroxide, and, together with rinsings from the Peligot tube, diluted to 100 c.c. The mercury is estimated in this solution by the iodometric method described by Rupp (A., 1908, ii, 1073). W. P. S.

Detection of Manganese and Zinc in the Presence of Phosphates or Oxalates. H. Wester (*Ber. Deut. Pharm. Ges.*, 1920, **30**, 142—145; *Pharm. Weekblad*, 1920, **51**, 381—385).—In the presence of phosphates, manganese is precipitated as phosphate when its solution is treated with ammonia or ammonium sulphide; the precipitate does not dissolve in an excess of the reagents, and ammonium chloride does not prevent the precipitation. When oxalates, but not phosphates, are present, the manganese remains in solution when treated with ammonia, etc. Zinc is not precipitated by an excess of ammonia and ammonium chloride, even in the presence of oxalates and phosphates. W. P. S.

Gravimetric Estimation of Manganese in Iron Ores and in the so-called Manganese Ores. Ballot (*Bull. Sci. Pharmacol.*, 1919, **26**, 514—516; from *Chem. Zentr.*, 1920, ii, 425).—The ore (0·25 gram, or 0·5—1 gram in the case of low manganese content) is fused with sodium peroxide in a nickel crucible. The cold, fused mass is dissolved in warm water (250 c.c.), and any manganate or permanganate is reduced by cautious addition of 95% alcohol. The filtered oxides of iron and manganese are dissolved by warming in a mixture of hydrochloric acid (10 c.c.), nitric acid (10 c.c.), and water (20 c.c.); the solution is treated with ammonia, diluted to 200 c.c., and heated to boiling. It is then treated with a suspension of barium carbonate in small quantities at a time until the supernatant liquor is no longer yellow. The precipitate is allowed to subside, and is then filtered. Excess of barium is removed from the combined filtrate and washings by means of ammonium sulphate, and the cold filtrate (which is diluted to 500—700 c.c.) is treated drop by drop with bromine until distinctly yellow in colour; ammonia is added in excess, and the mixture is heated to boiling. The precipitated manganese oxide is ignited and weighed as Mn_3O_4. H. W.

Volumetric Estimation of Manganese. Paul Nicolardot, Antoine Réglade, and Max Geloso (*Compt. rend.*, 1920, **170**, 808—810).—In using Knorre's method for the volumetric estimation of manganese, the manganese being precipitated by ammonium persulphate as the dioxide, and this precipitate redissolved in an excess of some reducing solution, which in its turn is titrated with standard permanganate, the theoretical factor for the calculation is 1 gram of iron = 0·4917 gram of manganese. In practice, it is found that this factor varies, owing to slight variation in the composition of the manganese dioxide precipitate. These variations are shown to be due to the presence of iron, the factor being 0·498 in the absence of iron and 0·4929 in the presence of 40% of iron. The acidity of the solution in which the pre-

cipitation occurs also has some influence, as when there is above 10% of sulphuric acid the precipitation of the manganese is incomplete. W. G.

The Gravimetric Estimation of Molybdenum as Sulphide. JAN ŠTĚRBA-BÖHM and JAROSLAV VOSTŘEBAL (*Zeitsch. anorg. Chem.*, 1920, **110**, 81—103).—The difficulties attending the estimation of molybdenum as sulphide can be avoided if the precipitation is carried out in presence of formic acid and certain precautions are taken. In presence of mineral acids, or even acetic or oxalic acid, precipitation is incomplete, on account of the formation of colloidal solutions. The molybdenum must all be present as molybdate, and any trace of reduced molybdenum must be first oxidised by means of nitric acid. The following procedure is recommended for carrying out a determination. A quantity of solution is taken containing from 0·1 to 0·3 gram of molybdenum trioxide, and is diluted with water to 200—300 c.c. Sufficient formic acid is then added to give a 5% solution of free acid. If less than this quantity of formic acid is used, colloidal solutions of molybdenum sulphide are liable to be formed, but more acid is not detrimental. If only small quantities of electrolytes are present in solution, it is advisable to add a small quantity of pure potassium chloride, up to 0·75%, calculated on the total volume of the solution. Directly the formic acid has been added, a rapid stream of hydrogen sulphide, free from acid, is passed through the solution, for the first half hour in the cold and then for one to one and a-half hours at 40—50°. Alternatively, the hydrogen sulphide may be passed for two hours into an alkaline solution of the molybdate (alkaline with ammonia or potassium hydroxide), the formic acid then added, and the solution heated for one hour on the water-bath. The precipitated molybdenum sulphide is washed by decantation, filtered on a Gooch crucible, and dried in a current of carbon dioxide, first at 100°, then at 250°. It is then cooled in the current of gas and weighed, since it is hygroscopic, in a weighing bottle. The product obtained when these conditions are observed is shown to have the exact composition MoS_3.

The sulphide prepared as above has a brownish-black to chocolate colour. Heated in air at 126°, it oxidises considerably, and in a current of oxygen, oxidation takes place at a lower temperature with incandescence, but complete oxidation to MoO_3 is only brought about with difficulty. The freshly precipitated sulphide can be digested with cold concentrated formic acid for twenty-four hours without any appreciable quantity of molybdenum passing into solution. The most delicate test for traces of molybdenum is shown to be the stannous chloride–thiocyanate–ether test, by means of which 1 part of molybdenum in 625,000 parts of water can readily be detected. E. H. R.

[Reactions of Osmium Tetroxide]. C. A. MITCHELL (*Analyst*, 1920, **45**, 125—127).—It was shown by Schlüttig and Neumann (*Die Eisengallustinten*, 1890, 16) that to produce a permanent

coloration with iron salts (that is, an ink) a substance must contain three hydroxyl groups in juxtaposition. The same rule applies to the colour reactions of osmium tetroxide, which yields an ink with gallotannic and gallic acids and with pyrogallol, but not with phenol or quinol. In very dilute solution osmic pyrogallate is at first violet, but almost immediately becomes greenish-blue, and when applied to paper gives a deep violet-black coloration. The reaction affords a sensitive test for osmium tetroxide, the distinctive blue coloration being obtained on adding a trace of solid pyrogallol to a solution containing a few drops of 1% osmium tetroxide solution. The vapour from boiling "osmic acid" solution will develop recent finger prints on paper, and conversely a slightly greasy finger print affords a test for osmium tetroxide, traces of organic substances left by the finger giving permanent grey to black colorations owing to the reduction of the osmium tetroxide to osmium. C. A. M.

Estimation of Trimethylene Glycol in Distilled Glycerol (Dynamite Glycerin) and in "First Runnings." C. A. ROJAHN (*Zeitsch. anal. Chem.*, 1919, **58**, 433—442).—The quantity of trimethylene glycol present may be calculated from the water content and specific gravity of the sample. The water is estimated by drying 2 grams of the sample on asbestos under reduced pressure over phosphoric oxide. Tables and graphs are given, and reference to these gives the percentage of trimethylene glycol directly. [See, further, *J. Soc. Chem. Ind.*, 1920, 314A.] W. P. S.

The Use of Aromatic Sulphochloroamides as Reagents. ALBERT BERTHELOT and M. MICHEL (*Bull. Sci. Pharmacol.*, 1919, **26**, 401—407; from *Chem. Zentr.*, 1920, ii, 425—426).—Neutral or alkaline solutions of sodium *p*-toluenedisulphochloroamide (chloramine-*T*) yield characteristic colorations, particularly with polyhydroxy-phenols and other substances of phenolic nature which, to a certain extent, depend on the concentration of the solutions, the quantity of reagents, the nature of the solvent, and the temperature, and, under definite conditions, are suitable for the characterisation of the individual substances. When, for example, 1 c.c. of a cold saturated solution of chloramine-*T* (about 15%) is treated with 4 c.c. of a 10% solution of the dihydroxybenzenes, a green coloration which becomes yellow is observed with resorcinol, whilst catechol gives an amethyst and quinol a currant-red coloration, which rapidly becomes brown; the effects are still noticeable at dilutions 1:10,000, 1:50,000, and 1:1000 respectively. α-Naphthol solution (1%, 4 c.c.) gives a violet shade in the cold, whilst β-naphthol gives no coloration in the cold, but an immediate brownish-red colour in boiling solution; the extreme dilutions are 1:50,000 and 1:100,000. Similar but less characteristic effects are produced by *p*-sulphodichloroaminobenzoic acid (halazone) in sodium carbonate solution and by *p*-toluenesulphodichloroamide (dichloramine-*T*) in dichloroethylene, which may be useful for the identification of substances insoluble in water. H. W.

Detection and Characterisation of Dextrose in Plants by a New Biochemical Method. EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1920, **170**, 631—635).—It has previously been shown (compare A., 1913, i, 542) that 82·6% of the dextrose in solution in 70% methyl alcohol is converted by emulsin into β-methyl glucoside. It is now shown that this change occurs in the presence of other sugars, such as mannose, lævulose, or arabinose, and the glucoside can be isolated in a crystalline form from the solution. This method can be used for the detection and estimation of dextrose in plants as follows. The dry plant material is extracted with boiling 80% alcohol, and the extract is evaporated to dryness. The residue is extracted with boiling ethyl acetate to remove resinous matters, and the residue is dissolved in a little water, and this solution is evaporated to dryness under reduced pressure. This final residue is dissolved in 70% methyl alcohol, and after the reducing power and rotation of the solution have been measured, emulsin is added and the liquid is left until no further change in the rotation occurs. The reducing power and rotation are again determined, and from these changes the amount of dextrose present in the original plant material can be calculated, allowing for 82·6% of it having been converted into β-methyl-glucoside. If required, the glucoside may be isolated from the methyl-alcoholic solution. W. G.

A System of Blood Analysis. Supplement I. A Simplified and Improved Method for the Estimation of Sugar. OTTO FOLIN and HSIEN WU (*J. Biol. Chem.*, 1920, **41**, 367—374). —In the method previously described (A., 1919, ii, 308) an error due to phenols is present. The authors now describe the preparation of a modified reagent, which gives no colour with phenols, but reacts with cuprous copper in acid solution. The criticisms which have been levelled at these methods on the grounds of reoxidation are discussed, and a special type of sugar tube is described, use of which prevents this source of error. The method is now considered to be without flaw. J. C. D.

Double Polarisation Methods for the Estimation of Sucrose, and a Suggested New Method. GEO. W. ROLFE and L. F. HOYT (*J. Ind. Eng. Chem.*, 1920, **12**, 250—253).—The rotatory power before inversion is determined on clarified solutions containing 3% of monochloroacetic acid, within fifteen minutes of the addition of the acid, no inversion occurring within this period at the ordinary temperature. A portion of the solution is then heated in a tightly stoppered flask for thirty minutes in boiling water, and the rotatory power is determined after the cooled solution has been kept for at least two hours. When the Ventzke sugar scale is used the sucrose is calculated by the usual Herzfeld formula with the substitution of 141·0 for the Herzfeld inversion constant. The results agree well with those obtained by the use of invertase as hydrolyst. [See also *J. Soc. Chem. Ind.*, 1920, May.] J. H. L.

Colorimetric Estimation of Glycogen. R. THIEULIN (*J. Pharm. Chim.*, 1920, [vii], **21**, 91—93).—Two c.c. of the neutralised glycogen solution are treated with two drops of iodine solution (iodine 1 gram, potassium iodide 2 grams, water 20 c.c.), and the reddish-brown coloration obtained is compared with those given by known amounts of glycogen under the same conditions.

W. P. S.

Specific Colour Reaction of Oxalates. V. MACRI (*Boll. Chim. Farm.*, 1920, **59**, 73).—The colour reaction for oxalates described by Caron and Raquet (A., 1919, ii, 438) was published earlier by the author (A., 1917, ii, 511) as a reaction for detecting manganese salts. The author now finds that addition of an oxidising agent, such as a hypochlorite, a dichromate, or hydrogen peroxide, is unnecessary, since agitation of a solution of a manganese salt in the hot with a little alkali hydroxide causes absorption of atmospheric oxygen and formation of higher oxides of manganese, these giving the characteristic red coloration with an oxalate. The reaction does not take place in acid solutions. T. H. P.

Approximate Estimation of Acetone and Acetoacetic Acid when present together in Urine. EMIL LENK and WALTHER HAHN (*Münch. med. Woch.*, 1917, **64**, 179; *Zentr. Biochem. Biophys.*, **19**, 262).—The Légal test was used for the detection of acetone and acetoacetic acid collectively and the Rimini ethylenediamine test for the detection of acetoacetic acid alone. The colours obtained in both tests diminished in intensity very rapidly. In applying the reactions the pigment solutions were diluted with water until the liquid was colourless. Strongly coloured samples of urine must first be decolorised. Directions for performing the tests, together with tabulated data, are given.

CHEMICAL ABSTRACTS.

A New Manometric Ureometer. PAUL BOBAY (*J. Pharm. Chim.*, 1920, [vii], **21**, 62—64).—A description is given of a new ureometer, the two principal features of which are a piston with a ground surface fitting into the base of the ureometer and the addition of a manometric tube to the graduated tube. The apparatus is figured in the original, and a detailed account of its structure and method of manipulation is given. W. G.

Estimation of Urea in Blood. A. SLOSSE (*Compt. rend. soc. biol.*, 1919, **42**, 1402—1404; from *Chem. Zentr.*, 1920, ii, 427).—Comparative estimations by Folin's and the hypobromite method gave practically always discordant results. Hypobromite not only decomposes urea, but also other nitrogenous substances of the blood, uric acid, creatine, creatinine, and amino-acids, which are invariably present, and, in pathological cases, frequently in such quantity that they cannot be neglected. The errors which can arise in the calculation of Ambard's constant from such data are particularly considered. H. W.

New Colour Reactions of Quinine. D. GANASSINI (*Il policlinico*, 1917, **24**, 344; *Arch. ital. biol.*, 1919, **69**, 73).—A yellow coloration, which becomes rose and finally purplish-red, is developed when a few drops of pyridine are added to a solution of quinine or of a quinine salt containing a slight excess of freshly prepared chlorine water. The colouring matter is almost insoluble in chloroform. Quinidine and euquinidine respond very feebly to the test; cinchonine and cinchonidine are inert.

The green coloration developed in the thalleoquinine test with bromine water and the minimal amount of ammonia becomes red after the addition of one or two drops of a freshly prepared 0·1% solution of potassium ferricyanide. The colouring matter is extracted by chloroform. CHEMICAL ABSTRACTS.

Indican in the Liquids of Organisms and its Investigation for the Identification of Urine. LEONE LATTES (*Arch. Farm. sper. Sci. aff.*, 1919, **28**, 5—16, 17—22).—The detection of indican (indoxyl) in a spot forms a good, practical means for identifying urine, although theoretically the reaction is not absolulutely specific. The reaction answers even when the spot has undergone putrefactive and similar changes. Failure of the reaction does not, however, exclude urine, since the spot may have experienced accidental alteration, besides which some urines may be either very poor in, or quite free from, indoxyl. T. H. P.

Estimation of Hæmoglobin by the Acid Hæmatin Method. LOUIS BERMAN (*Arch. Intern. Med.*, 1919, **24**, 553—556).—The Sahli method is modified by the use of a standard prepared daily, the use of 0·1*N*-hydrochloric acid as a diluent throughout, and heating the test to boiling for one minute after the first matching to accelerate and complete the reaction, after which the final dilution and reading are made. CHEMICAL ABSTRACTS.

A Comparative Study of Various Methods for the Estimation of Hæmoglobin. FRIEDA S. ROBSCHEIT (*J. Biol. Chem.*, 1920, **41**, 209—225).—When in Sahli's method the colour tubes accompanying the instrument are used, very inaccurate results may be obtained because of the decided variance in colour density of the standard tubes, due to fading. Palmer's method (A., 1918, ii, 88) is good, provided the standard solutions are freshly prepared, whilst Newcomer's method (A., 1919, ii, 179) gives good results with the glass 0·96 mm. in thickness. With the heavier glass, 1·02 mm. in thickness, the colour match is only approximate. A method is presented which applies Palmer's procedure to Sahli's principle. The standards for this process remain unappreciably changed for eleven months. J. C. D.

Estimation of Methæmoglobin in Blood. WILLIAM C. STADIE (*J. Biol. Chem.*, 1920, **41**, 237—241).—The method depends on the fact that both hæmoglobin and methæmoglobin are changed quantitatively into cyanohæmoglobin by dilute solutions of potassium

cyanide. The colour of the latter substance is a brilliant orange-red, and is very suitable for colorimetric comparison. The total amount of the hæmoglobin aud methæmoglobin is estimated by this colorimetric method, whilst the hæmoglobin is determined separately from the oxygen capacity, employing Van Slyke's method for the gasometric estimation of that pigment. J. C. D.

The Detection of Blood in Fæces. P. N. VAN ECK (*Pharm. Weekblad*, 1920, **57**, 218—227).—A critical discussion of the methods which have been proposed. A bibliography of the subject is appended. W. S. M.

Benzidine as Chromogen in Biological Oxidation Reactions. M. KJÖLLERFELDT (*Pflüger's Archiv*, 1918, **172**, 318—334).—The value of benzidine hydrochloride solutions for these tests is dependent on the method of preparation, and on the age of the solution. The author recommends a *N*/200-solution of the pure hydrochloride as giving the best results. J. C. D.

Volumetric Estimation of the Alkalinity of Blood; Influence of Protein Substances on this Estimation. Its Value. RENÉ CLOGNE (*J. Pharm. Chim.*, 1920, [vii], **21**, 49—62).—The method recommended is as follows. Five c.c. of the blood or serum are introduced into a 50 c.c. graduated flask and diluted to 40 c.c. with a saturated solution of sodium chloride. The mixture is heated on a boiling water-bath, and to it 6 c.c. of *N*/10-nitric acid are added. After three minutes the liquid is cooled and made up to the mark with more sodium chloride solution and filtered. Forty c.c. of the filtrate are titrated with *N*/10-sodium hydroxide solution, using phenolphthalein as an indicator. The average of the results obtained from the blood of fourteen normal individuals, very slightly wounded, was an alkalinity equivalent to 3·17 grams of sodium hydroxide per litre. The average for ten men suffering from severe shock was 2·79 grams per litre, and for eight men severely wounded and suffering from gas gangrene was 2·86 grams per litre.

Further investigation showed that the results obtained depended, to a considerable extent, on the amount of *N*/10-acid added, the variations obtained being due to the presence of protein. The results obtained with a solution of egg-albumin and with blood serum indicate that the alkalinity results are probably a function of the protein present rather than of the alkaline bases. W. G.

Apparatus for Measurement of Oxydase and Catalase Activity. R. B. HARVEY (*J. Gen. Physiol.*, 1920, **2**, 253—254).—A description of a modified Bunzel apparatus (A., 1914, ii, 508). The source of error in the earlier forms of apparatus is a failure to absorb carbon dioxide which is produced. This error is removed in the new design by using an alkali hydroxide tube. J. C. D.

General and Physical Chemistry.

Refraction and Dispersion of Carbon Dioxide, Carbon Monoxide, and Methane. CLIVE CUTHBERTSON and MAUDE CUTHBERTSON (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 152—159).—The *refractivities and dispersion coefficients* of the three gases were determined with a Jamin refractometer. For the green mercury line ($\lambda = 5461$), the refractivities, reduced to 0° and 76 cm., were as follows: carbon dioxide, 4505; carbon monoxide, 3364; methane, 4415. In all cases, the value of $(\mu - 1) . 10^7$ is given. Tables giving the dispersion are supplied. The refractions and dispersions of the carbon atom calculated from the results do not show any agreement, the figures for the relative numbers of electrons and the free frequencies being also discordant. It is concluded that the forces which control the motion of a dispersion electron in an atom are profoundly affected by the proximity of another atom in combination with it. If the two atoms are of the same element, as in the molecules of diatomic gases, a similar, but probably simpler, change occurs in such a way that the free frequencies in both atoms are originally the same and are altered to the same extent.

J. R. P.

The Variation with Pressure of the Wave-length of the Rays of the Bands of Cyanogen. A. PEROT (*Compt. rend.*, 1920, **170**, 988—990).—By varying the pressure from atmospheric pressure down to 2—3 cm. of mercury, it is shown that the values of $d\lambda/\lambda$ for the bands 4197 and 3883 are $1 \cdot 8 \times 10^{-6}$ and $1 \cdot 4 \times 10^{-6}$ respectively.

W. G.

Spectrum of Copper. W. M. HICKS (*Phil. Mag.*, 1920, [vi], **39**, 457—481).—A theoretical paper in which the copper spectrum is treated in the same way as the spectra of silver and gold (A., 1919, ii, 441). Strong, well-defined sets are given for the orders $m = 2$, 3 in both the S and D sets and for the first order of P. Those for S (2) are in the red and in step with those of silver. The others show the Zeeman patterns proper for their respective types. These may therefore be adopted definitely as normal series lines. In the higher orders, the intensities fall off more rapidly and irregularly than usual, and there is also evidence for numerous displacements. These are apparently the cause of the low intensities and the large number of weak lines. In consequence, the determination of the S and D limits, with any exactness, from the series lines alone is rendered impossible.

J. F. S.

Effect of Solvent on the Ultra-violet Absorption Spectrum of a Pure Substance. F. O. RICE (*J. Amer. Chem. Soc.*, 1920, **42**, 727—735).—The effect of the solvents, water, ethyl alcohol, heptane, and chloroform, on the ultra-violet absorption spectrum

of many ketones has been investigated. It is shown that all aliphatic ketones, except acetone and methyl ethyl ketone, follow Beer's law, that is, the molecular extinction is independent of the concentration and solvent. With acetone and methyl ethyl ketone there are deviations when ionising solvents are used, due to partial disruption of the associated molecules. Kundt's rule, which states that with increasing refractivity of solvent the absorption band moves towards the red, holds good if it is regarded as a rough generalisation. When a pure substance is dissolved in an ionising solvent, the absorption centre moves towards the ultra-violet; if a pure substance is dissolved in a neutral, non-ionising solvent, the absorption centre is unaffected or moves toward the red end of the spectrum. It is probable that this is a general rule which holds for all classes of absorbing substances. J. F. S.

Light Absorption and Fluorescence. V. The so-called Molecular Rotational Frequencies of Water. E. C. C. BALY (*Phil. Mag.*, 1920, [vi], **39**, 565—577. Compare A., 1916, ii, 363). —A theoretical paper in which, from the atomic frequency of oxygen, 2.4531×10^{11}, found by the author for this substance in sulphur dioxide (*loc. cit.*), and the measurements of Sleator (*Astrophys. J.*, 1918, **48**, 125), the author is able to calculate the central frequencies of the water absorption bands. The agreement between the calculated values and the values observed by Sleator is good, the maximum difference being $0.0022\,\mu$, whilst the average difference is $\pm 0.00074\,\mu$. The results obtained for the system of frequencies possessed by the molecules of sulphur dioxide and water definitely establish the existence of simple relationships between the three sets of frequencies, molecular, intramolecular, and atomic. The atomic frequencies are characteristic of the individual atoms, the molecular frequencies are characteristic of the molecule as a whole, and the intramolecular frequencies are characteristic of groups of atoms in the molecules. J. F. S.

Activation of Hydrogen Peroxide by Light. HARRY A. CURTIS (*J. Amer. Chem. Soc.*, 1920, **42**, 720—724).—Solutions of aniline-green and magenta are not bleached when exposed to the light of a quartz mercury lamp, neither are they bleached by the addition of 3% hydrogen peroxide to them until the mixture is exposed to the light. The rate of bleaching of the mixtures was followed by means of a Hellige-Leitz colorimeter, and curves are given. To be sure that the bleaching in light was due to hydrogen peroxide and not to ozone, solutions of the dyes were submitted to the light while a stream of oxygen was bubbled in; there was no bleaching in this case. Hence it appears that the oxidising power of hydrogen peroxide with respect to the bleaching of dyes is increased by exposing the mixture to light of short wave-lengths. J. F. S.

Chemical Induction in Photographic Development. I. Induction and the Watkins Factor. S. E. SHEPPARD and G. MEYER (*J. Amer. Chem. Soc.*, 1920, **42**, 689—700).—The Lainer

effect, acceleration of development of photographic plates by dilute solutions of iodides, has been investigated, and shown to affect chiefly organic developers of low reduction potential, such as quinol. It is also shown that the principal effect is to overcome the induction with such organic developers, consequently increasing the Watkins factor. The effect is regarded as due to the increased adsorption and complex formation between silver haloid and developer. The bearing of this on the theory of development is discussed. There is, in addition, a fogging action by dilute solutions of potassium iodide on silver bromide emulsions, which is attributed to nucleus infection of the grain. J. F. S.

Stereoisomeric Transformations and Polymerisation of Organic Substances under the Influence of Light and their Constitution. P. R. Kögel (*Photo. Korr.*, 1919, **56**, 368—380; from *Chem. Zentr.*, 1920, i, 489).—The acetylene and cyanogen groups are photopolymeric. The methyl group with a double bond (ethylene group) is both photostereoisomeric and photopolymorphic. The same is true of the corresponding compounds of nitrogen. The orthoquinonoid formula is assigned to anthracene on account of its ability to undergo polymerisation. The sensitiveness of diazonium compounds to light depends on their tendency to photostereoisomeric transformation. The disposition of the chief valencies in the stereoisomeric and polymeric methyl group is the same as that in the pallidogenic methyl group.
H. W.

Photosynthesis and the Electronic Theory. Henry H. Dixon and Horace H. Poole (*Sci. Proc. Roy. Dubl. Soc.*, 1920, **16**, 63—77).—Electrical measurements made with metallic plates coated with chlorophyll in different ways and illuminated from different sources of light indicate that those wave-lengths of light which are effective in photosynthesis are unable, to any appreciable extent, to expel electrons from the leaf pigment complex, and hence cannot in this way produce ionisation or bring about reactions external to the pigment. The action apparently occurs within the molecule of the chlorophyll itself, the atomic groups of the leaf pigment entering into the action of photosynthesis and participating in the combinations and decompositions which ultimately lead to the formation of carbohydrates and the evolution of oxygen. W. G.

The Scattering of γ-Rays. K. W. Fritz Kohlrausch (*Physikal. Zeitsch.*, 1920, **21**, 193—198).—A pencil of γ-rays, from 0·8 gram of radium chloride, after passing through absorption screens, falls on a block of carbon, aluminium, zinc, tin, or lead as radiator at 0·5 metre distance, and the secondary γ-radiation at different angles α with the direction of incidence is examined as regards intensity and penetrating power over a circle of 0·64 metre radius, by means of an ionisation chamber. The decrease of the hardness and intensity of the secondary γ-radiation with increasing

values of a was confirmed. The change of hardness was shown to be due to the existence in varying proportion of two types of secondary rays, S_1 and S_2, corresponding with the two types of primary, K_1 and K_2. The results showed that S_1 was a scattered K_1 radiation of the same hardness, and that probably S_2 is similarly a scattered K_2 radiation. None of the S_1 radiation is scattered through more than 90°, but the S_2 radiation extends in the direction of incidence as well as in that of emergence. Tables are given showing the distribution of the intensity of the radiation over the complete circle, and the results are compared with the theory of Debye and shown to be in qualitative agreement with it, particularly as regards the asymmetry of distribution found for the radiation in the directions of incidence and emergence. The probable wave-length of the γ-rays is discussed in the light of these results. F. S.

The Properties of Reinforcing Screens with respect to *X*-ray Spectra, and a Decomposition of the β-Line of the *K* Spectrum of Tungsten. MAURICE DE BROGLIE (*Compt. rend.*, 1920, **170**, 1053—1056).—The effect of reinforcement increases rapidly with the penetration of the rays, and the luminous excitation of the screen is thus itself dependent on the absorption band of the heavy metal (tungsten in the calcium tungstate used) which the screen contains. With a screen coated with cadmium tungstate there was no apparent selective reinforcement due to the cadmium.

Using special conditions to obtain the *K* spectrum of tungsten it was found that the line β_1, $\lambda = 0{\cdot}1844$ Ångstrom, was split into two components, the one with the greater wave-length being the more feeble. The difference between these two components is given by $d\lambda = 0{\cdot}0007$ Ångström. W. G.

Mass-spectra of Chemical Elements. F. W. ASTON (*Phil. Mag.*, 1920, [vi], **39**, 611—625).—A full account is given of the structure and method of operating a positive ray spectrograph, which is capable of producing a focussed positive ray spectrum (mass spectrum). The results of a provisional analysis of eleven chemical elements, hydrogen, helium, carbon, nitrogen, oxygen, neon, chlorine, argon, krypton, xenon, and mercury are summarised. These show that only five—hydrogen, helium, carbon, nitrogen, and oxygen—are "pure" elements, the others being composed of various numbers of isotopic constituents. The number of isotopes n and their masses m in order of intensity are: hydrogen, $n=1$, $m=1{\cdot}008$; helium, $n=1$, $m=4$; carbon, $n=1$, $m=12$; nitrogen, $n=1$, $m=14$; oxygen, $n=1$, $m=16$; neon, $n=2$, $m=20$, 22 (21); chlorine, $n=2$, $m=35$, 37 (39); argon, $n=(2)$, $m=40$ (36); krypton, $n=6$, $m=84$, 86, 82, 83, 80, 78; xenon, $n=5$, $m=(128$, 131, 130, 133, 135); mercury, $n=(5)$, $m=(197$—200, 202, 204). The values enclosed in brackets are provisional. With the exception of those due to H_1, H_2, and H_3, all masses measured, allowing for multiple charges, are exactly whole numbers within the error of experiment (O = 16). The lines due to hydrogen indicate that the

mass of this element is greater than unity on this scale, and is in good agreement with the chemical value 1·008. J. F. S.

The Determination of the Radioactivity of Spring Waters. OTTOMAR NÜRNBERGER (*Physikal. Zeitsch.*, 1920, **21**, 198—203).—A comparison of the different methods and instruments used by H. W. Schmidt, Engler and Sieveking, Mache and Meyer, Kohlrausch and Loewenthal, for the estimation of the radium emanation in spring waters, and the conditions to be observed to obtain trustworthy and comparable results. F. S.

Course of the Transformation Process of Isomeric Ions. GEORG VON HEVESY and LÁSZLÓ ZECHMEISTER (*Zeitsch. Elektrochem.*, 1920, **26**, 151—153).—It is shown by the radioactive indicator method that a dynamic equilibrium exists between bivalent and quadrivalent lead ions in glacial acetic acid solution, and in consequence it follows that electrons can pass of themselves, in certain circumstances, from one ion to an isomeric ion and also to an electrode. J. F. S.

Ionisation and Activity of Largely Ionised Substances. ARTHUR A. NOYES and DUNCAN A. MACINNES (*J. Amer. Chem. Soc.*, 1920, **42**, 239—245).—A theoretical paper in which the experimental results of MacInnes and Parker (A., 1915, ii, 510, 734), Ellis (A., 1916, ii, 369), and Noyes and Ellis (A., 1918, ii, 27), in connexion with the electrodes $Ag + AgCl \mid LiCl \mid LiHg \mid LiCl \mid AgCl + Ag$ and $Hg + HgO \mid KOH \mid K$ in $Hg \mid KOH \mid HgO + Hg$ are discussed. It is shown that in the case of potassium chloride, lithium chloride, hydrochloric acid, and potassium hydroxide the activity coefficient decreases with increasing concentration much more rapidly than does the conductivity–viscosity ratio, the differences amounting to from 7% to 15% at $N/10$- and from 5% to 18% at $N/5$-concentration. In the case of all the substances except potassium chloride, the activity-coefficient, unlike the conductivity–viscosity ratio, passes through a pronounced minimum in the neighbourhood of $N/5$ and afterwards increases rapidly at the higher concentrations. Even potassium chloride, according to Harned's data (A., 1918, ii, 597), has a minimum activity-coefficient about $2N$. The activity-coefficient even at moderate concentrations varies considerably with the nature of the substance; thus its value in $0·5N$-potassium chloride is 65%, lithium chloride 73%, hydrochloric acid and potassium hydroxide 77%. Thus it follows that the conductivity ratio can no longer be regarded as even an approximate measure of the activity of the ions of highly ionised substances in their mass action and thermodynamic relations. The activity varies with the concentration differently in the case of different substances and, at present, it can only be determined empirically for each substance with the aid of chemical equilibrium measurements, *E.M.F.*, and freezing-point measurements. It is also shown that the ionic activity-coefficients cannot be proportional to or mainly determined by the fraction of

the substance ionised; for this fraction could not increase wit increasing concentration unless the ionising power of the mediu becomes much greater at moderate concentrations, and even the it could not become greater than unity, as is actually the case wit the activity-coefficient of hydrochloric acid in concentrations abov 2*N*. J. F. S.

The Constancy of Electrical Conductivity of Gase during Chemical Reactions. MAX TRAUTZ and FRIEDRIC AUGUST HENGLEIN (*Zeitsch. anorg. Chem.*, 1920, **110**, 237—289 —To determine whether or no ionisation occurs during chemica reactions, a number of purely gaseous reactions were studied. Th apparatus used consisted essentially of a glass reaction vessel c cylindrical form containing a cylindrical condenser, both surfac of which were of graphite or glass. The outer surface was co nected by a platinum wire sealed into the wall of the reaction vess to a high-tension battery, the inner surface similarly to a quadra electrometer set. Preliminary experiments showed that none of th materials employed, matte glass surfaces, platinum wire, graphi or paraffin, had any appreciable influence on the velocity of th reaction $2NO + Cl_2 \rightleftharpoons 2NOCl$. When the reaction vessel was fille with dry air and the outer electrode connected to the high-tensio battery, a small charge appeared on the inner electrode an increased gradually to a maximum value, in spite of the mo careful insulation of the two electrodes. This charge, it w proved, is a result of the ionisation of the gas. It increases wi increasing pressure and is greater for chlorine than for air. T ionisation of the air in the enclosed vessel was considerably great than that which has been found by other methods for free atm spheric air.

The reactions studied were the following: $2NO + Cl_2 \rightleftharpoons 2NOC$ $2NO + Br_2 \rightleftharpoons 2NOBr$; $2HBr + Cl_2 \rightleftharpoons 2HCl + Br_2$; $Cl_2 + H_2$ 2HCl. In no case could evidence of ionisation during the reacti be obtained. Pinkus stated (A., 1918, ii, 286) that ionisati could be detected in the case of the first reaction when chlori was in excess. His results could not be confirmed, and were pro ably due to frictional electricity generated by the sudden rush gas into the reaction vessel. It is concluded that during gaseo reactions at moderate temperatures, even when the heat of reacti is great, no free electrons are produced.

Manometric experiments were made to determine whether, wh gaseous hydrogen chloride, bromide, or iodide is mixed respective with gaseous chlorine, bromine, or iodine, any hydrogen trihalo is formed. The results in each case were negative. E. H. R.

Disruptive [Sparking] Potential in Carbon Dioxide High Pressures. C. E. GUYE and P. MERCIER (*Arch. Sci. ph nat.*, 1920, [v], **2**, 30—49, 99—124).—The authors measur the sparking potential in carbon dioxide at high pressures wi great accuracy. At atmospheric pressure, with plane electro

45 mm. diameter, the sparking potential for the same distance is greater in air than in carbon dioxide, although this difference appears to vanish at small distances. Exposure to ultra-violet light diminishes the potential to a greater extent in carbon dioxide than in air. The action of ultra-violet light is inappreciable at pressures greater than 10 atm. For distances from 2 to 5 mm. the potential increases linearly with the pressure up to 10 atm. For 1 mm., and especially for 0·5 mm., this relation no longer holds, although the deviations are very small. The results depend on the form of the electrodes. The results are explained by an accumulation of positive and negative ions in the vicinities of the electrodes before the spark passes. This leads to the deviation from Paschen's law at small distances, and also causes the energy of the spark to increase, giving rise to a more intense spark. J. R. P.

Absorption of Gases in the Electric Discharge Tube. F. H. Newman (*Proc. Physical Soc.*, 1920, **32**, 190—195. Compare A., 1914, ii, 703).—A continuation of experiments previously described (*loc. cit.*). Nitrogen is absorbed by both sodium and potassium under the influence of an unidirectional discharge in a discharge tube. The experiments were made at various pressures (8·1—1·0 mm.), and with the metals as cathode and anode respectively. In the case of sodium, it is shown that the amount of absorption is greater when it is the cathode. In the case of potassium, less gas is absorbed than with sodium. Using the liquid alloy of sodium and potassium, there was no difference in the rate of absorption when the temperature was raised from 50° to 200°, but above this temperature the rate of absorption increased very much. After the discharge had been interrupted and the alloy was heated to above 300°, there was no evolution of gas, so that in all probability moderately stable nitrides of sodium or potassium, or both, had been formed. J. F. S.

Reproducible Liquid Junction Potentials: The Flowing Junction. Arthur B. Lamb and Alfred T. Larson (*J. Amer. Chem. Soc.*, 1920, **42**, 229—237).—The reproducibility and constancy of liquid junction potentials has been investigated in the case of gelatin diaphragm, parchment diaphragm, and flowing junctions. The experiments show that liquid junctions formed between the bearing surfaces of ground-glass stoppers, in gelatin diaphragms, and in parchment paper diaphragms with 0·1*N*-hydrochloric acid and potassium chloride solutions are not constant and reproducible to closer than 0·2—0·4 millivolt. Somewhat more constant results are obtained with parchment diaphragms on stirring. Fresh junctions in 5 mm. tubes give potentials reproducible in 0·1*N*-solutions to about 0·03—0·06 millivolt when the electrolyte is prevented from oscillating, but with *N*-solutions variations of 0·3 millivolt occur. Stirred junctions sometimes give very constant potentials, but these are quite different from that produced by a flowing junction, and, moreover, they differ, depend-

ing on the method of stirring. A flowing junction, obtained simply by an upward current of the heavier electrolyte meeting a downward current of the lighter electrolyte in a vertical tube at its point of union with a horizontal outflow tube, or by allowing the lighter electrolyte to flow constantly into a large volume of the heavier electrolyte, even with *N*-solutions, gives potentials constant and reproducible to 0·01 millivolt. An apparatus in which such flowing junctions may be obtained is depicted in the paper.

J. F. S.

A Lead Standard Cell. M. G. Mellon and W. E. Henderson (*J. Amer. Chem. Soc.*, 1920, **42**, 676—689. Compare Henderson and Stegeman, A., 1918, ii, 54).—Cells of the type

$$PbHg\,|\,PbSO_4\,||\,Na_2SO_4,10H_2O(sat.)\,||\,Hg_2SO_4\,|\,Hg,$$

of which the *E.M.F.* and stability have previously been studied (*loc. cit.*), were constructed, in which the electrolyte was replaced by solutions, both saturated and unsaturated, of the sulphates of potassium, lithium, magnesium, nickel, cobalt, zinc, manganese, cadmium, and copper. These cells have been examined with respect to their *E.M.F.*, reproducibility, and constancy. It is shown that the cell with sodium sulphate, constructed in 1917 (*loc. cit.*), has the same value as freshly made cells. It is shown that saturated cells containing the sulphates of nickel, cobalt, zinc, or manganese are substantially as reproducible and as constant as those containing sodium sulphate. This constancy is usually reached in four to five days after preparation, and these cells appear to possess the characteristics necessary for a standard cell. The *E.M.F.* of the cell which has become constant seems to be nearly independent of the soluble sulphate used. The value of the *E.M.F.* for cells containing sodium or nickel sulphate is practically the same, 0·96466 volt and 0·96430 volt respectively, whilst those of cells containing cobalt, zinc, and manganese sulphate are very close together, but are slightly higher than those of the first-named cells; they have values 0·96478, 0·96477, and 0·96478 volt respectively. Saturated cells containing the sulphate of lithium, magnesium, or cadmium are neither reproducible nor constant, although the *E.M.F.* has approximately the same value as the constant cells. Saturated cells containing potassium sulphate are neither reproducible nor constant; the mercurous sulphate in them is distinctly hydrolysed, and the *E.M.F.* is markedly higher than that of the other cells. Saturated cells containing copper sulphate agree well among themselves, but are not constant. The *E.M.F.* is approximately one-third that obtained for the other cells, which indicates that the lead of the amalgam replaces the copper, and a copper amalgam is produced. Unsaturated cells containing the sulphates of sodium, zinc, nickel, cobalt, and manganese are just as reproducible as the saturated cells, they have the same *E.M.F.*, and are constant for a time, and then exhibit a decreasing *E.M.F.* Unsaturated cells containing the sulphates of lithium, magnesium, and cadmium have approximately the same *E.M.F.* as the saturated cells, and they

are equally unsatisfactory. Attempts to ascertain the cause of the unsatisfactory nature of these cells were without result.

J. F. S.

A New 0·1N-Calomel Electrode Design. A. E. Koehler (*J. Biol. Chem.*, 1920, **41**, 619—620).—This type of electrode was designed to overcome the changes in normality which the solutions in other patterns of instruments are apt to show. The apparatus is illustrated, and has been used for two months without showing any change in *E.M.F.* J. C. D.

Platinised Glass Electrodes for Electrolytic Estimations. G. Meillère (*J. Pharm. Chim.*, 1920, [vii], **21**, 311—313).—Electrodes suitable for many purposes may be made by fusing a small piece of platinum wire into a glass tube, watch-glass, etc., then varnishing the glass with a solution of platinum chloride and an essential oil in methyl alcohol, and heating the glass until all organic matter has been oxidised. Several successive coatings may be applied in order to obtain a suitable layer of platinum on the glass. In some cases, it is advantageous to etch the glass with hydrofluoric acid before the platinum varnish is applied.

W. P. S.

Conduction of Electricity by Free Electrons and Carriers. III. Migration Velocity of Particles moving under Forces in Viscous Media. P. Lenard, W. Weick, and Hans Ferd. Mayer (*Ann. Physik*, 1920, [iv], **61**, 665—741. Compare *ibid.*, 1900, 312).—A theoretical paper in which relationships are deduced for expressing and calculating the velocity of ions and other carriers of electricity in various media. Values are calculated for the radius (r) and the number of molecules of water (n) combined with the following ions in aqueous solution: $H^{\cdot}$, $n=1·4$, $r=0·9\times10^{-8}$ cm.; OH', $n=2·5$, $r=1·4\times10^{-8}$ cm.; $Li^{\cdot}$, $n=19$, $r=5·0\times10^{-8}$ cm.; $Na^{\cdot}$, $n=12$, $r=4·2\times10^{-8}$ cm.; $K^{\cdot}$, $n=7$, $r=3·1\times10^{-8}$ cm.; $Rb^{\cdot}$, $n=6$, $r=2·9\times10^{-8}$ cm.; $Cs^{\cdot}$, $n=6$, $r=2·8\times10^{-8}$ cm.; F', $n=11$, $r=3·9\times10^{-8}$ cm.; Cl', $n=6$, $r=3·2\times10^{-8}$ cm.; Br', $n=6$, $r=3·0\times10^{-8}$ cm.; I', $n=6$, $r=2·9\times10^{-8}$ cm. It is shown that there is a distinct parallelism between the value of n and the temperature-coefficient of the migration velocity. J. F. S.

Alternating Current Electrolysis. S. Marsh (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 124—144).—Solutions of sulphuric acid and barium hydroxide have been electrolysed with alternating current of varying frequency by means of electrodes of gold, platinum, and nickel. In the case of platinum foil electrodes and sulphuric acid, the amount of evolution of gas decreases rapidly with time, and eventually no more gas is evolved. The amount evolved decreases with increasing frequency of the current; when thin platinum electrodes were used, the amount was less, but no simple relationship between the volume of gas evolved and the thickness

of the electrode was observed. The time–volume curves resemble the saturation curves obtained in radioactive measurements. With gold electrode and sulphuric acid, the rate of evolution of gas falls off rapidly with time, but for frequencies less than 48, gas is still given off at the electrodes for a much longer time than with platinum, and the total volumes of gas are considerably smaller than in the case of platinum. In the case of nickel, a copious evolution of hydrogen occurred for twenty minutes, beyond which the experiment could not be continued, owing to solution of the electrode. With barium hydroxide as electrolyte, the rate of evolution decreases with time and with increasing frequency, but the time–volume curves are practically straight lines. The volume of gas liberated is much greater than in acid solutions. Gold and platinum behave very similarly in barium hydroxide solution, but nickel only evolves the smallest quantity of hydrogen with a frequency of 60 cycles, and even with 40 cycles the volume of gas is too small to measure. Two suggestions are put forward to explain the phenomena: (i) the oxidation of the electrode, coupled with subsequent reduction by the hydrogen of the next half-period; (ii) the absorption and adsorption of hydrogen by the electrode, coupled with recombination with oxygen of the next half-period. These processes are not mutually exclusive, and it is possible that both agencies are operative in degrees varying with the metal employed. J. F. S.

Electro-endosmosis and the Preparation of Solid Alkali-metal Amalgams. Sumner B. Frank and James R. Withrow (*J. Amer. Chem. Soc.*, 1920, **42**, 671—675).—A number of experiments on electro-endosmosis show that it is modified by the type of porous cell used, but that an increased voltage and current density will always cause it to take place. Using solutions of potassium chloride, potassium sulphate, strontium chloride, and calcium acetate, endosmosis is always observed if the voltage is more than 8. The phenomenon is made very visible by the following experimental arrangement. The solution, saturated by preference, is placed in a beaker fitted with any form of platinum anode, and a porous cell is immersed to a depth of about 5—10 mm. in the solution, and about 50 grams of mercury, which serves as cathode, poured in. Contact is made with the mercury in the usual way, and a voltage of 20—25 is applied. In about sixty minutes, the solution will have entered and filled the porous pot to a height of about 3—4 cm. In these experiments, solid amalgams of potassium and strontium were obtained, but in the case of calcium, no amalgam was obtained, only a mixture of calcium hydroxide and finely divided mercury. J. F. S.

Electrical Characteristics of Dye Colloids. Rudolf Keller (*Kolloid Zeitsch.*, 1920, **26**, 173—178. Compare A., 1919, ii, 491).—A continuation of the previous discussion (*loc. cit.*), in which the reason for the discrepancy between the author's experiments and the statements of many text-books is given. It is shown

that the statement of the text-books refers to dilute solutions of dyes where the substances in solution are ion disperse systems and the coloured cation naturally travels to the cathode, whereas the ıuthor's experiments were carried out with concentrated dye soluions which were colloid disperse systems and the cation wandered n the opposite direction. J. F. S.

Influence of Molecular Constitution and Temperature ɔn Magnetic Susceptibility. IV. Further Applications of :he Molecular Field. A. E. OXLEY (*Phil. Trans.*, 1920, [*A*], **220**, 247—289. Compare A., 1914, ii, 424; 1915, ii, 219).—A theoretiɑl paper in which the discussion previously published is continued. The applications of local molecular forcive, in diamagnetic, paramagıetic, and ferromagnetic media, have been extended to interpret the ıltimate strength of crystalline and vitrous media. It is to be ·xpected, since the permanent set which occurs prior to breaking s due to slipping along the cleavage planes within the crystal ;rains, that the material will be fractured when the applied mechınical stress is equal to that produced internally by the local nolecular forcive. The internal stress within the material is of the ·rder 2×10^9 dynes per sq. cm., which is approximately the mean ·f the ultimate strengths of crystalline and vitreous media. As a onsequence of this internal stress, the energy per unit volume will ·e 2×10^9 ergs, and this energy is a measure of the latent heat of usion per c.c. It is found that the elastic constants of a variety of erromagnetic, diamagnetic, and paramagnetic media are of the ame order, several diamagnetic and paramagnetic media even sur·assing steel in their power to resist distortion. The energy change ʼhich occurs on crystallisation is compatible with a volume change f the same order of magnitude as that accompanying crystallisaion, and the change of volume on crystallisation may therefore be ıterpreted as a magneto-striction effect of the local molecular ɔrcive. The magneto-striction effect depends on molecular orienta.on, which is proportional to the square of the magnetic forcive. A hysical interpretation has been given of the large values of the ·efficients N and a_r' of the molecular fields in ferromagnetic and iamagnetic crystalline media respectively. These coefficients are ıe reciprocals of the limiting local susceptibilities of the media nder field strengths equal to the respective molecular fields. The ·cal susceptibility of a diamagnetic molecule is comparable with ıat of a ferromagnetic molecule, and the two vary in the same ay with field strength and temperature. In diamagnetic media, ɔwever, magnetic hysteresis will be inappreciable, since the molerle as a whole possesses a zero magnetic moment. Mechanical ysteresis in diamagnetic media will be of the same order as in rromagnetic media. It has been previously shown (*loc. cit.*) that ıe magneton may be a constituent of the diamagnetic hydrogen olecule. This idea may be extended to carbon and the hydrorbons in general, where the molecular susceptibility can be rectly calculated from the atomic susceptibilities of the component

atoms. The results in other cases are unconvincing, but the fact that departures from the additive law occur in these cases leads to the conclusion that some disturbing influence has been overlooked.

J. F. S.

Magnetic Properties of Nickel–Copper Alloys. R. GANS and A. FONSECA (*Ann. Physik*, 1920, [iv], **61**, 742—752).—The magnetic susceptibility of nickel–copper alloys has been measured over a range of concentrations from 20·3% nickel to 60·2% nickel at temperatures from −230° to 55°, and the transformation point determined for each concentration. A series of susceptibility measurements are also given for 15° for the whole of the alloys. The results show that the Tammann rule (A., 1909, ii, 16) is not true in the present case, and that ferromagnetic substances dissolved in non-magnetic crystals yield ferromagnetic alloys. Copper–nickel alloys form a complete series of mixed crystals except over the range 45—50% nickel, in which nickel crystals saturated with copper and copper crystals saturated with nickel exist. The present results are analogous to those obtained for cobalt–copper alloys, except that in this case the gap in the mixed crystal series is considerably larger.

J. F. S.

Magnetic Susceptibility of Antimony and Bismuth: Form of the Magneton. HECTOR ISNARDI and RICHARD GANS (*Ann. Physik*, 1920, [iv], **61**, 585—590).—The specific susceptibility of bismuth and antimony has been determined by the Weiss method, using fields lying between $H=1029$ Gauss and $H=13680$ Gauss. The results show that the magnetic susceptibility of these metals is independent of the strength of the field, and that the apparent dependence found by Honda and Owen (A., 1910, ii, 686; 1912, ii, 425) is probably due to the presence of iron as an impurity in the material and also to errors of measurement. The following mean values are found: bismuth, $-\chi \cdot 10^{-6} = 1{\cdot}346$; antimony, $-\chi \cdot 10^{-6} = 0{\cdot}8138$. From the Gans theory it is shown that the principal moments of inertia of the magneton are identical. This result is obtained only for bismuth and antimony, but judging from the measurements of Honda and Owen it is probably true for other elements.

J. F. S.

Specific Heat of Carbon Dioxide and Steam. W. T. DAVID (*Phil. Mag.*, 1920, [vi], **39**, 551—553).—A theoretical paper in which the author advances the suggestion that the specific heat of steam and carbon dioxide depends not only on the temperature, but also on volume and density. At any particular temperature the greater the volume of the gas the greater its specific heat, and the greater the density the less its specific heat. In a previous communication (A., 1911, ii, 1046) the author has shown that carbon dioxide and steam emit radiation in appreciable quantity in the neighbourhood of 1000° and very strongly in the neighbourhood of 2000°. Consequently, the specific heat of these gases may be

expected to vary slightly with volume and density at 1000° and very markedly at 2000°. J. F. S.

Secondary Valencies and Fusibility. ARRIGO MAZZUCCHELLI (*Gazzetta*, 1920, **50**, i, 93—97).—According to Nernst ("Kinetische Theorie der Materie," Leipzig, 1913), the varying fusibilities of the elements are explainable by their different numbers of primary and secondary valencies, the reciprocal attractions of which keep the atoms fixed in the crystalline network characteristic of the solid state. The author extends this conception to the interpretation of certain apparently contradictory regularities in the fusibility of metallic and non-metallic compounds.

With the latter the fusibility diminishes as the number of atoms in the molecule increases, the more complicated molecules appearing to find greater difficulty in assuming the condition of irregular movement characteristic of liquids; the same rule holds for the volatility, a measure of which is afforded by the critical temperature. The correlation between molecular complexity and melting or boiling point is most marked in homologous series of carbon compounds, and is, indeed, so general for non-metallic compounds that divergences are utilised as criteria of polymerisation in the liquid state.

With compounds of the metals, on the other hand, fusibility and volatility increase with increase in the complexity of the molecule.

To explain the different behaviour of non-metallic and metallic compounds the author advances the following considerations. From Nernst's assumption that the heavy metals are relatively infusible because their numerous primary and secondary valencies hold the atoms firmly in the crystalline network, the conclusion is drawn that combination of the metallic atom with an increasing number of oxygen or other non-metal atoms results in increasing saturation of the valencies in the interior of the molecule. Thus, the number of valencies available to maintain the molecules united in the crystalline aggregate is diminished and the fusibility consequently increased. In other words, entry of oxygen, chlorine, etc., introduces into the molecule that internal saturation of the valencies to which oxygen, chlorine, etc., owe their fusibility. This explanation applies, not only to binary compounds, but also to those of higher orders and to hydrated salts. Further, it is not invalidated by the information furnished in recent years by *X*-ray diffraction spectra, which show that the various atoms are distributed almost uniformly in the crystalline network. T. H. P.

Apparatus for the Determination of Melting Points. L. M. DENNIS (*J. Ind. Eng. Chem.*, 1920, **12**, 366—368).—The apparatus is similar to that described by Thiele (A., 1907, ii, 330), but the lower portion is inclined downwards; the "rising" portion of the loop is of narrower diameter, and enters the main tube at an angle. It is claimed that there is better circulation of the sulphuric acid and a more uniform temperature can be maintained. W. P. S.

Fractionation Flask for the Distillation of Froth Liquids. EMIL LENK (*Chem. Zeit.*, 1920, **44**, 330).—The lo end of a condenser is fused on to the neck of an ordinary f tionating flask at a point below the outlet tube of the latter, is then bent upwards to form a reflux condenser. These two out from the flask are connected with a pump, the communication be controlled by a three-way tap, so that a vacuum can be produ in either direction. In distilling a viscous liquid the reflux denser is first exhausted, and the froth will then rise into it the liquid subsequently fall back into the flask. When the liq in the flask is boiling steadily a vacuum is created in the ot direction and the distillation continued. To facilitate the ret of substances solid at the ordinary temperature from the ref condenser, hot water may be circulated through the cooling jac The inner tube of the condenser is constricted at intervals to fo a series of pear-shaped bulbs. C. A. M

A Simple Distillation Apparatus for Separation of Wat GEO. W. WALKER (*Chem. News*, 1920, **120**, 222).—In distill solvents such as benzene and chloroform, which contain water distilling flask with two necks is used. One neck is connected rubber tubing with a condenser, the other by rubber tubing wit flask cooled in water. At the commencement of the distillation, tube leading to the condenser is closed by a clip, and the wa allowed to distil off into the flask. The first clip is then opened, the tube leading to the flask closed by a second clip. Distillat of the solvent then proceeds. J. R. I

The Energy of the Atomic Linkings in Diamond in Aliphatic Hydrocarbons. K. FAJANS (*Ber.*, 1920, [*B*], 643—665).—The heat of combustion of a saturated aliph hydrocarbon may be regarded as the result of the heat formation of a carbon hydrogen bond (x), that of a simple linking in compounds (y) [the similar linking in diamond be denoted by y'], the heat of formation of liquid water from 1 gr atom of atomic hydrogen and molecular oxygen (v), and the h of formation of gaseous carbon dioxide from 1 gram atom of ato carbon (monatomic carbon vapour) and molecular oxygen (z). the special cases of propane and ethane the expressions may written: $-8x+8v-2y+3z=526{\cdot}7$ and $-6x+6v-y+2z=37$ by subtraction of which there is obtained $-2x+2v-y+z=1$ Cal. as the expression of the increase in the heat of combustion to the addition of the methylene group. Since z and v are indep dent of the substance under investigation, it follows that magnitude $y+2x$ is subject to but little variation, which is m simply explained by the hypothesis that x and y are constant first approximation, that is, the energy of a simple C–C or C–H linking is practically the same in different saturated aliph hydrocarbons. Further, an examination of the available data various hydrocarbons leads to the conclusion that the energy of

C–C linking in hydrocarbons is practically uninfluenced by the further attachment of the C atoms to other C or H atoms. If x and v are eliminated from the first two equations, the expression $z-2y=96{\cdot}5$ Cal. is obtained; the number is rather considerably influenced by slight experimental errors in the data on which it is based, but a consideration of a large number of suitable estimations leads to the equation $z-2y=98\pm8$. The recent work of Langmuir, Isnardi (A., 1915, ii, 738) and Franck, Knipping, and Krüger (this vol., ii, 145) allows v to be evaluated at $74{\cdot}4\pm2{\cdot}8$ Cal. Now the heat of combustion of the diamond is the result of two factors (*a*) the heat required to convert solid diamond into monatomic carbon vapour [heat of sublimation], and (*b*) the heat of combustion of the vapour (z) to carbon dioxide. Using Roth's values, one obtains $z-2y'=94{\cdot}4$ Cal. Since, however, $z-2y=98\pm8$, it follows that $y'-y=2\pm4$ Cal., from which it is deduced that the heat of formation of a C–C linking in saturated hydrocarbons is practically the same as that in diamond. Since v is known, y is practically equal to y', and $2y'$ represents the difference in energy between solid diamond and monatomic carbon vapour, the problem of dissecting the heat of formation of hydrocarbons resolves itself into the estimation of the heat of sublimation of diamond. This has been estimated by Fajans (*Zeitsch. Physik*, 1920, **1**, 101) to be 287 Cal. The following values can thus be deduced: $z=381$ Cal., $y=137{\cdot}5$ Cal., $v=74{\cdot}4$, and $x=117$ Cal. The data are applied to the calculation of the heats of formation of a series of hydrocarbons, both from diamond and hydrogen and from the atomic substances; in the latter case large positive values are always indicated, and it is interesting to note that the formation of the C=C and C≡C linkings is associated with the development of 252 and 365 Cal. respectively, whereas the production of the C–C bond only evolves 136 Cal. Strictly speaking, it should be observed that the values assigned to the energy of the various linkings are only valid when all other available valencies of the carbon atoms are saturated.

Similar considerations are applied to the combustion of carbon in oxygen. The relatively smaller development of energy which is associated with the first stage of the oxidation is only apparent; when the heat of sublimation of diamond is taken into account, the equation may be written $C_{vapour}+\frac{1}{2}O_2=CO+314$ Cal., whilst $CO+\frac{1}{2}O_2=CO_2+67{\cdot}8$ Cal.

The paper concludes with a criticism of the recent communications of von Weinberg (A., 1919, i, 314) and Padoa (A., 1919, ii, 97), for details of which the original must be consulted.

H. W.

The Energy of Atomic Linking in Graphite and in the Aromatic Hydrocarbons. A. L. von Steiger (*Ber.*, 1920, **53**, [*B*], 666—680 Compare Fajans, preceding abstract).—The investigation was undertaken with the object of referring the unique position of aromatic ring systems in organic chemistry to

the peculiar nature of their carbon atoms. It has been shown by Debye and Scherrer (A., 1917, ii, 437) from a consideration of the crystalline structure of graphite that the carbon atoms in the latter may be regarded as tervalent if the energy of the fourth bond is neglected on account of its smaller order of magnitude. Proceeding in the same manner as Fajans (*loc. cit.*), the author finds that, for purposes of calculation, the carbon atoms of purely aromatic hydrocarbons which are made up of simple or condensed six-carbon rings may be regarded as tervalent, and that all C–C linkings are equivalent. It is further found that the energy of the C–C linking in graphite is very nearly the same as in aromatic hydrocarbons. Since the molar heat of sublimation of graphite has been calculated (Fajans, *Zeitsch. Physik*, 1920, **1**, 107), it is therefore possible to calculate the heat of combustion of an aromatic hydrocarbon, the constitution of which is known. It is interesting to note that the energy of the C–C and C–H groups in aromatic is greater than in aliphatic hydrocarbons, the respective values being 187·3 and 137·5 for the former and 137·7 and 117 Cal. for the latter.

Basing his ideas on the equality of energy of the C–C linking in graphite and in the purely aromatic hydrocarbons, the author traces a close analogy between the six-membered rings of the carbon planes in the former and the six-ring system of the latter, and is thus led to the following conception of the constitution of aromatic ring systems. The latter are composed of carbon atoms, which have the same disposition of valencies as the carbon atoms in graphite. The distance from one another is approximately $1·45 \times 10^{-8}$ cm. The chief valencies lie in a plane and make an angle of 120° with one another. The existence of free subsidiary valencies of a smaller order of magnitude in the aromatic ring is very probable, and, if the analogy with graphite may be pushed so far, they must be considered as placed at right angles to the plane of the six-carbon ring. H. W.

Pressure and Temperature-coefficients, Volume, and Heat Effects in Bivariant Systems. P. H. J. Hoenen (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 526—530).—A mathematical paper in which equations are developed by which the composition may be calculated of each phase of a system having n components in which there may be n co-existing phases and in which p and T are independent variables. Further equations are developed for calculating the relation between the pressure- and temperature-coefficients for the transition of the components from one phase to another in a system of n components and l phases when $n \equiv l$; further expressions give the heat effects and the volume changes which accompany the transition. J. F. S.

Van der Waals's Force of Cohesion. P. Debye (*Physikal. Zeitsch.*, 1920, **21**, 178—187).—A theoretical paper in which, from a consideration of electrical attraction of two molecules for one another, expressions are derived whereby the van der Waals's constant b may be calculated. Further expressions are developed

whereby the surface tension and the Eötvös constant may be calculated. J. F. S.

The Falling Sphere Viscosimeter. WILLIAM HOWIESON GIBSON and LAURA MARY JACOBS (T., 1920, **117**, 473—478).

Orientation of Molecules in Surfaces, Surface Energy, Adsorption, and Surface Catalysis. V. Adhesional Work between Organic Liquids and Water. WILLIAM D. HARKINS, GEORGE L. CLARK, and LATHROP E. ROBERTS (*J. Amer. Chem. Soc.*, 1920, **42**, 700—712. Compare A., 1917, ii, 238, 239; 1916, ii, 222, 223).—A table is given which contains the free surface energy, the adhesional work per sq. cm., the interfacial free energy, the surface adhesion, and the densities of about seventy organic liquids. Of these liquids about thirty-four have been freshly investigated. The data presented are in keeping with the view that the molecules at interfaces are oriented. It is assumed from the formulæ that carbon disulphide has a symmetrical molecule and ethyl mercaptan an unsymmetrical molecule. The cohesional work is much greater in the former case than in the latter, 62·8 ergs per sq. cm. instead of 43·6, whilst the adhesional work between water and carbon disulphide is much less (55·8 ergs per sq. cm.) than it is between water and mercaptan (68·5 ergs per sq. cm.). These facts are readily explained by the orientation theory. Thus the attraction between octane and water is relatively small, the adhesional work being only 43·76 ergs. The octane molecule contains 26 atoms, and yet the introduction of one oxygen atom at the end of the chain more than doubles the adhesional work, and increases it to 91·77 ergs. A similar introduction of one oxygen atom into *iso*pentane increases the adhesional work towards water from 36·9 to 92·5, an increase of 150%. The substitution of an amine group for a hydrogen atom at the end of a chain causes a similar increase, as also does the substitution of –COOH, –CN, =CO, or any similar groups. The great magnitude of the effect, when it is considered that the addition of 1 atom to 26 causes an increase of 132%, is strong evidence that the oxygen is turned towards the water. It is found that in only three cases out of fifty-eight is the cohesional work of an organic liquid greater than its adhesional work toward water. The three substances are carbon disulphide, ethylene dibromide, and acetylene tetrabromide. The excess of the adhesional over the cohesional work increases as the symmetry of the molecule decreases. This is also strong evidence in favour of the orientation theory. The benzene hydrocarbons are more polar than the paraffin hydrocarbons. Aniline is found to be extremely polar in comparison with most of the organic liquids. The polar characteristics of the benzene derivatives are distributed much more over the whole molecule than is the case with the paraffin derivatives. The total surface energy and the free surface energy are not due to the orientation of the molecules, but to the stray surface field, and this is decreased by the orientation.

J. F. S.

Adsorption and Solubility. E. F. Lundelius (*Kolloid Zeitsch.*, 1920, **26**, 145—151).—The adsorption of iodine from solutions in carbon tetrachloride, carbon disulphide, and chloroform by blood charcoal has been determined at 19—20°. The results are plotted as absorption isotherms for the surface of 1 gram of charcoal. In general, the results show that the adsorption is inversely proportional to the solubility. The adsorption of vapours of toluene, carbon disulphide, carbon tetrachloride, chloroform, benzene, and hexane by blood charcoal has also been determined, and it is shown that approximately equal volumes of the various substances are adsorbed from their saturated vapours, from which it follows that the thickness of the layer of adsorbed material is the same in all cases examined. J. F. S.

Relationship between the Height of Capillary Rise, the Time, and the Concentration in the Capillary Rise in Filter Paper. Hans Schmidt (*Kolloid Zeitsch.*, 1920, **26**, 152—159. Compare A., 1913, ii, 721; 1919, ii, 185).—The height to which solutions of glycerol and dextrose of various concentrations rise in filter paper has been determined at temperatures 15—17°. Also the rate of rise has been ascertained in all cases. The results show that the constant of the velocity of capillary rise is inversely proportional to the viscosity of the solution. It is also shown that it is possible, from the relationship between the time required by a given solution to rise to a definite height and that of pure water, to calculate approximately the concentration of the solution.

J. F. S.

Cause of the Influence of Ions on the Rate of Diffusion of Water through Collodion Membranes. I. Jacques Loeb (*J. Gen. Physiol.*, 1920, **2**, 387—408).—In this paper it is shown that in electrical endosmose through a collodion membrane the influence of electrolytes on the rate of transport of liquids is the same as in free osmosis. Since the influence of electrolytes on the rate of transport in electrical endosmose must be ascribed to their influence on the quantity of electrical charge on the unit area of the membrane, it follows that the same explanation holds for the influence of electrolytes on the rate of transport of water into a solution through a collodion membrane in the case of free osmosis. It may, therefore, be concluded that when water is separated from a solution of an electrolyte by a collodion membrane, the rate of diffusion of water by free osmosis is accelerated by the ion with the opposite sign of charge to that of the watery phase of the double layer, and that it is retarded by ions with like charge. The influence of the ions of an electrolyte in raising or lowering the charge on the unit area of the solution side of the membrane, compared with that on the water side, will determine whether osmosis is positive or negative. A further conclusion is that in lower concentrations of many electrolytes the density of electrification of the double layer increases with an increase in concentration, whilst in

higher concentrations of the same electrolytes it decreases with an increase in concentration. In the case of a number of electrolytes the turning point lies about $M/512$ or $M/256$. J. C. D.

Extension of Braun's Law. P. H. J. Hoenen (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 531—535).—A mathematical paper in which it is shown that Braun's law, which has the form $(\partial x/\partial p)_T : (\partial x/\partial T)_p = T\Delta V/Q$, is a particular case of a more general law which is developed in the present work. The general law is formulated thus:

$$(\partial x/\partial p)_T \, . \, Qx/T + (\partial x/\partial T)_p \, . \, \Delta V_x + (\partial y/\partial p)_T \, . \, Q_y/T + (\partial y/\partial T)_p \, . \, \Delta V_y + \text{etc.} = 0,$$

in which $(\partial x/\partial p)_T$ and $(\partial y/\partial p)_T$ are the pressure-coefficients of the solubility of x and y respectively, $(\partial x/\partial T)_p$ and $(\partial y/\partial T)_p$ are the temperature-coefficients, ΔV_x and ΔV_y the differential increase in volume due to x and y respectively. J. F. S.

Determination of the Dissociation Constants of some Mineral Acids. Emile Blanc (*J. Chim. Phys.*, 1920, **18**, 28—45).—The degree of dissociation of a number of acids and the degree of hydrolysis of the sodium salts of some of them have been determined by means of conductivity, potential, and the indicator methods. The following values for the degree of hydrolysis are found at 25° for the salts named: sodium phosphate 0·012N is hydrolysed 34·1%; disodium hydrogen phosphate, 0·012N, 0·066%; sodium phosphite, 0·0075N, 0·021%; sodium dihydrogen arsenite, 0·0104N, 0·394%; sodium arsenate, 0·002N, 8·0%; disodium hydrogen arsenate, 0·002N, 0·0455%; sodium selenite, 0·0108N, 0·379%; sodium hydrogen tellurite 0·0075N, 0·0022%; sodium tellurite, 0·0075N, 0·773%; sodium hydrogen tellurate, 0·0093N, 0·117%; sodium tellurate 0·0093N, 13·97%; potassium molybdate, 0·00975N, 0·359%; and potassium tungstate, 0·0162N, 0·011%. The following new dissociation constants have been calculated from the experimental results: phosphorous acid, $K_2 = 2 \times 10^{-5}$; arsenic acid, $K_2 = 4 \times 10^{-5}$; $K_3 = 6 \times 10^{-10}$; selenious acid, $K_1 = 2 \times 10^{-3}$, $K_2 = 5 \times 10^{-8}$; tellurous acid, $K_1 = 2 \times 10^{-3}$, $K_2 = 1 \times 10^{-8}$; telluric acid, $K_1 = 6 \times 10^{-7}$, $K_2 = 4 \times 10^{-11}$. J. F. S.

A Model for Demonstrating Crystal Structure. Herbert P. Whitlock (*Amer. J. Sci.*, 1920, [iv], **49**, 259—264).—The model, which is used for demonstrating the spatial distribution of the atoms in a crystal as revealed by the X-ray method of Bragg, consists of a number of thin glass rods mounted vertically in a double diaphragm perforated with holes arranged in a symmetrical pattern, a centred square pattern, for instance, for cubic, tetragonal, and orthorhombic crystals, or an equilateral triangular pattern for hexagonal and rhombohedral crystals. The atoms are represented by spherical wooden beads bored with a hole to fit the rods. The beads are spaced accurately on the rods to represent different groupings of atoms, and are fastened in position by a drop of glue.

Beads of different colours are used to represent different kinds of atom. E. H. R.

Differentiation between Molecular and Colloidal Solutions. WA. OSTWALD (*Kolloid Zeitsch.*, 1920, **26**, 138—140).—It is suggested that molecular and colloidal solutions may be differentiated by an examination of the ice produced by freezing them. In the colloidal solutions it is suggested that a difference in composition of successive horizontal layers may be found, due to the settling of the colloidal particles during the freezing. J. F. S.

Automatic Sedimentation Recorder and its Use in some Colloid-chemical Problems. SVEN ODÉN (*Kolloid Zeitsch.*, 1920, **26**, 100—121).—An apparatus is described whereby the rate of sedimentation of a suspension may be automatically recorded. The apparatus consists of a thin gold-plated disk, which is suspended to one arm of a sensitive balance and hangs inside a cylinder of nearly the same diameter in which the suspension is placed. The precipitation plate is exactly balanced by weights on the other pan, and when a small quantity of the suspended matter falls on it, it sinks; this operates an electric contact, which by means of relays causes a small iron pellet to be thrown on the weight pan. The precipitation plate is thus raised, and the contact broken. Each time the two pans are of exactly the same weight a mark is made on a slowly rotating paper coil which marks the time. Thus the weight and time, and consequently the rate of sedimentation, are known. This apparatus has been used in determining the mean and actual diameter of suspensoid particles in the case of silver bromide, the aggregation time, and the dependence of the aggregation time on the concentration of the particles and the electrolyte concentration. J. F. S.

Coagulating Power of some Electrolytes. (MLLE.) N. BACH (*J. Chim. Phys.*, 1920, **18**, 46—64).—The relative coagulating power of ions of the alkali metals and the halogens has been determined by means of a new method, which consists in measuring the opacity number of the electrolyte. The opacity number is the number of c.c. of a normal solution of the electrolyte which will produce a definite turbidity in a colloidal solution. This quantity can be determined with great precision, and consequently the method is well suited to this purpose. The coagulating power of an electrolyte is the reciprocal of the opacity number. It is shown that the ratio of the opacity numbers of two electrolytes depends only on the nature of the colloid, and it may be that it is even independent of this. The opacity numbers are all referred to that of potassium chloride as unity. It is found that the coagulating power of the alkali ions follows the order: $Cs^{\cdot} > Rb^{\cdot} > NH_4^{\cdot} > K^{\cdot} > Na^{\cdot} > Li^{\cdot}$ and the halogen ions $Cl' > Br' > I'$. Other things being equal, an alkali ion coagulates a negative colloid more powerfully and protects a positive colloid more effectually the more electropositive it is, and a halogen ion coagulates a positive colloid and

protects a negative colloid more strongly the more electronegative it is. The coagulating power is always much more marked than the protecting power. In the case of the halogen ions the difference between the discharge potentials is proportional to the difference between the coagulating power. The coagulating power of potassium chloride mixed with hydrochloric acid, potassium hydroxide, barium chloride, potassium sulphate, lanthanum chloride, sodium citrate, and potassium ferrocyanide has also been measured, and it is shown that both the coagulating power and the protecting power are additive. It is also shown that colloidal solutions are extremely sensitive to traces of multivalent impurities. J. F. S.

Direct Experimental Determination of the Concentration of Potassium and Sodium Ions in Soap Solutions and Gels. CYRIL SEBASTIAN SALMON (*T.*, 1920, **117**, 530—542).

Emulsions. I. A New Method of Determining the Inversion of Phases. SHANTI SWARUPA BHATNAGAR (T., 1920, **117**, 542—552).

Non-, Uni-, and Bi-variant Equilibria. XX. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 542—554. Compare A., 1917, ii, 454; this vol., ii, 169).—A further theoretical paper dealing with the conditions of equilibrium in non-variant, uni-variant, and bi-variant systems. The present paper deals with the equilibria of n components in n phases, in which the quantity of one of the components approaches the zero value, and the influence of a new substance on a non-variant (P or T) equilibrium. J. F. S.

Equilibrium Conditions of the Reaction between Silver Sulphide and Hydrogen. F. G. KEYES and W. A. FELSING (*J. Amer. Chem. Soc.*, 1920, **42**, 246—251).—The equilibrium $Ag_2S + H_2 \rightleftharpoons 2Ag + H_2S$ has been investigated at the temperatures 750°, 811°, and 890° absolute, by the method and with the apparatus previously described by Keyes (A., 1912, ii, 627). The following values of the equilibrium constant were obtained: 749·15°, $K = 0·359$; 811·25°, $K = 0·325$; and 889·63°, $K = 0·278$. From the results it is shown that the heat of the reaction is to be expressed $Ag_2S + H_2 = 2Ag + H_2S + 2410$ cal. The equilibrium constant, between 750° and 890° absolute, is expressed as a function of the temperature by means of the expression $\log_{10} K = 525·8/T - 1·1470$. The corresponding expression for the decrease in free energy over the same temperature range is $-\Delta F = RT \log_e K = 2408 - 5·253T$. J. F. S.

Heterogeneous Equilibria between Aqueous and Metallic Solutions. Interaction of Mixed Salt Solutions and Liquid Amalgams. VI. Ionisation Relations of Sodium and Potassium Chlorides, Bromides, and Iodides in Mixtures. L. S. WELLS and G. McP. SMITH (*J. Amer. Chem. Soc.*, 1920, **42**, 185—205. Compare A., 1918, ii, 67; 1917, ii, 455). —The equilibrium between sodium and potassium amalgams and

mixtures of sodium and potassium chloride, bromide, and iodide respectively, has been investigated. It is shown that at a fixed total salt concentration the value of the equilibrium constant $C_c = nk = (K_{Hg})(NaX)/(Na_{Hg})(KX)$ decreases with increasing concentration of the amalgam. At fixed amalgam and total salt concentrations, but with varying salt ratio, the value of C_c is constant. At a fixed amalgam concentration the value of C_c decreases with the increasing concentration of the mixed (equivalent) salt solution. Ion-fraction calculations are put forward for aqueous binary salt mixtures containing the salts in equivalent proportions. It is found that the simple potassium-ion fraction decreases, whilst the sodium-ion fraction correspondingly increases with the increasing total salt concentration. These changes take place the more rapidly the higher the average atomic weight of the halogens in the mixture. These results are not in keeping with the view that at equivalent concentration salts of the same type are ionised to the same extent. The general results of the work are readily explained in terms of Werner's theory concerning the formation and dissociation of higher order compounds. J. F. S.

Rate of Corrosion of Aluminium. GEORGE HERBERT BAILEY (*J. Soc. Chem. Ind.*, 1920, **39**, 118—120T).—A measure of the extent to which a sample of aluminium is corroded, in terms of the metal so corroded per day per 100 sq. cm. of surface, is given by $CR = 9/8(S + w - W)$, where W is the weight of the sheet employed, w its weight after exposure, and S the weight of the precipitate obtained after ignition. The variation of CR with the concentration of the corrosive solution employed at 12° is shown by a number of curves in which log CR is plotted against concentration. In the case of sodium, potassinm, and barium hydroxides the curves are straight lines showing increasing attack as the concentration increases, whereas the ammonia curve rises to a maximum and then falls off. For the mineral acids, CR is fairly steady up to $0{\cdot}30N$; in the case of hydrochloric acid the curve then rises very steeply, whilst the curves for nitric and sulphuric acids rise more gradually to maximum values and then fall. At ordinary temperatures corrosion ceases, for example, in the case of sodium hydroxide or hydrochloric acid, when the solution has become exhausted, but at higher temperatures, in the neighbourhood of 100°, attack continues indefinitely, with formation, in the case of hydrochloric acid, of colloidal basic salts. The formation of a protective coating causes the rate of attack to fall off considerably with time, more rapidly in the case of impure metal than with purer specimens. The protective film, in the case of ammonia, is only about 0·01 mm. in thickness, but it has considerable insulating power for high-tension electric currents. E. H. R.

The Reversible Reaction between Iron and Steam. E. SCHREINER and F. B. GRIMNES (*Zeitsch. anorg. Chem.*, 1920, **110**, 311—334).—Measurements of the equilibrium pressures of water-vapour and hydrogen in the reaction $Fe + H_2O \rightleftharpoons FeO + H_2$ were

made between 595° and 920°, using an apparatus similar to that first employed by Deville (*Compt. rend.*, 1870, **70**, 1105, 1205). It was shown that refinements in the apparatus introduced by other workers with the object of accelerating the diffusion of the gases in the reaction tube were unnecessary. The values obtained for $K = p_{H_2O}/p_H$ were in good agreement, starting from either side of the equilibrium position. There are considerable discrepancies between the results obtained by different workers, particularly at high temperatures, where, in all cases, the value of K is much lower than that calculated from thermodynamic principles. The discrepancies are probably due to reactions in the solid phase, for example, the formation of solid solutions between iron and ferrous oxide, or to the different behaviour of different modifications of iron. Further experiments are suggested to test this hypothesis.

E. H. R.

The Influence of the Solvent on the Velocity of Reaction between certain Alkyl Iodides and Sodium β-Naphthoxide. HENRY EDWARD COX (T., 1920, **117**, 493—510).

Hydration as an Explanation of the Neutral Salt Effect. ARTHUR JOHN WILSON (*J. Amer. Chem. Soc.*, 1920, **42**, 715—720). —The addition of 120 grams of sodium chloride to chrome tanning iquor (17 grams of Cr_2O_3 as sulphate per litre) increases the hydrogen-ion concentration about 50% and prevents the liquor from anning skins. Other experiments show that the amount of 0·1N-sodium hydroxide necessary to produce a precipitate of basic chromic salts increases if certain neutral salts are added to the iquor, thus: 10 c.c. of the untreated liquor required 3·7 c.c., but he addition of 0·04 gram of sodium chloride increased the amount o 6·8 c.c. Using many salts the order of increase in the amount of sodium hydroxide required increases with the salts, potassium chloride (4·0 c.c.) < ammonium chloride < sodium chloride < magnesium chloride < magnesium sulphate < sodium sulphate < ammonium sulphate (11·6 c.c.). The author attributes this action to the hydration of the added salt with consequent increase of the acid concentration, and he calculates the number of molecules of water combined with one molecule of the salt in the case of sodium chloride for a number of dilutions; the following values are given: 4N, 10·9; 3N, 13·2; 2N, 16·3; N, 20·5; N/10, 5·5; N/100, 26·1; N/1000, 26·2; infinite dilution, 26·2. The hydrations of all the salts used are calculated for infinite dilution, and the following values obtained: potassium chloride, 15; ammonium chloride, 15; lithium chloride, 35; barium chloride, 50. J. F. S.

The Action of Finely Divided Gases. C. ZENGHELIS (*Compt. rend.*, 1920, **170**, 883—885).—The author attributes the action of gases in the nascent state to the fact that they are in an extremely finely divided state. This explanation is based on the fact that he has been able to obtain numerous reductions, such as of solutions of mercuric chloride, potassium chlorate, or potassium

nitrate, or of a saturated aqueous solution of carbon dioxide, by passing hydrogen, generated in an external vessel, into the liquid through filter-paper or dialysis parchment. Under somewhat similar conditions he has performed certain oxidations and brought about the combination of nitrogen and hydrogen in the cold. The reactions are, of course, slower under these conditions than when the nascent gases are used, because the state of division is probably not so fine. W. G.

Catalysis. XIII. Contact Potentials and Dielectric Capacities of Metals, in Relation to the Occlusion of Hydrogen, and Hydrogenation. WILLIAM CUDMORE McCULLAGH LEWIS (T., 1920, **117**, 623—638).

Catalytic Oxidation at Solid Surfaces: Some Factors Controlling the Rate of Hydrogenation of Ethylenic Compounds in Presence of Nickel. E. FRANKLAND ARMSTRONG and T. P. HILDITCH (*J. Soc. Chem. Ind.*, 1920, **39**, 120—124T).—The hydrogenation of ethyl cinnamate and of anethole in presence of nickel at 140° and 180° takes place at practically a linear rate throughout the greater part of its course, when a free current of hydrogen is maintained. When, however, the reaction is carried out in a closed system, the rate gradually falls off and the curve approximates to the logarithmic type. This is due solely to the decreasing concentration of the hydrogen, caused by the gradual accumulation of gaseous impurities from the hydrogen and, to a less extent, from the organic compound. The results confirm the authors' previous conclusions drawn from a study of the hydrogenation of olive, cottonseed, linseed, and whale oils (A., 1919, ii, 403; this vol., ii, 102). The hydrogenation of anethole gives rise to a crystalline by-product which has not been identified, but ethyl cinnamate is reduced quantitatively to ethyl β-phenylpropionate.
E. H. R.

Catalytic Hydrogenation with Protected Hydrosols. ERIC K. RIDEAL (*J. Amer. Chem. Soc.*, 1920, **42**, 749—756).—The effect of a protective colloid on the reaction velocity of a hydrogenation process in the presence of colloidal platinum and palladium has been studied, and the results lead to the conclusion that the protecting colloid functions as a peptising agent, in agreement with Bancroft's hypothesis (A., 1917, ii, 129). The addition of a small quantity of a palladium sol to a platinum sol greatly enhances its activity, and it is suggested that promoter action may in part be due to peptisation. The mechanism of catalytic actions in the presence of colloidal metal appears to conform rather to the diffusion hypothesis than to the colloid reactant complex theory. Abnormalities are equally explicable on the single-layer theory as on the view that the retardation of diffusion is caused by the products of the reaction. The various reactions were studied by means of the influence of the colloidal metals on solutions of sodium phenylpropiolate in the presence of gum arabic. J. F. S.

Rhythmic Mercury-Hydrogen Peroxide Catalysis. TOKIHARU OKAYA (*Proc. Phys. Math. Soc. Japan*, 1919, [iii], **1**, 283—294).—The theory deduced by the author in connexion with the rhythmic precipitation of silver chromate in gelatin and the rhythmic evolution of carbon monoxide during the dehydration of formic acid (A., 1919, ii, 504) has been applied to the rhythmic mercury-hydrogen peroxide catalysis, and verified experimentally. An equation is developed, by means of which the accumulation constants, H', are shown to be constant throughout the reaction.

CHEMICAL ABSTRACTS.

Structure of Matter and the Quantum Theory. F. H. LORING (*Chem. News*, 1920, **120**, 181—184, 193—196, 205—207, 217—219).—Atomic weights are derived from that of hydrogen, $H=1\cdot008$, by what is called an "electromagnetic multiplication table":

If	$1\times1\cdot008=1\cdot008$ (a),
and	$4\times1\cdot008=4\cdot000$ (d),
then	$2\times1\cdot008=2\cdot004$ (b),
and	$3\times1\cdot008=3\cdot002$ (c),

where a = hydrogen; d = helium; b = nitrogen sub-atom; c = fluorine sub-atom. Carbon and oxygen should then be: $C=3He=12\cdot000$; $O=4He=16\cdot000$. Nitrogen and fluorine are: $N=3He+b=14\cdot004$; $F=4He+c=19\cdot002$. The changes of mass in the table are assumed to have their origin in energy changes during the condensation of the constituents of the complex atoms. If helium atoms are assumed as units of atomic structure (4·000), and atomic outriders, or sub-atoms, a, b, c, d, added, the results are said not to differ appreciably from the accepted atomic weights. The main results obtained in connexion with the quantum theory and positive rays are summarised. The author speculates on atomic structure, isotopes, and valency. J. R. P.

The Atomic Weight of Hydrogen and its Relation to Prout's Hypothesis. ALOIS BILECKI (*Zeitsch. anorg. Chem.*, 1920, **110**, 335—338).—It has been shown in a previous paper (A., 1917, ii, 197) that the atomic weights of a number of elements are multiples of $n=0\cdot307692\dot{3}$, where $n=16/52$. It is now shown that $n/40$, $=0\cdot007692307$, is a number of fundamental importance. A critical examination of published determinations of the atomic weight of hydrogen ($O=16$) establishes the value 1·0077 for this quantity. The fraction 0·0077, it is pointed out, is almost exactly equal to $n/40$. E. H. R.

The Atomic Weight of Phosphorus in Relation to that of Silver. ALOIS BILECKI (*Zeitsch. anorg. Chem.*, 1920, **110**, 339—340).—The fundamental number n (preceding abstract) becomes $n_1=0\cdot30735042\dot{7}$ when $Ag=107\cdot88$ instead of 108. The atomic weight of phosphorus, determined through the halogens with respect to $Ag=107\cdot88$, is practically identical with $101n_1=31\cdot04235$. E. H. R.

The Relation of the Atomic Weight of Barium to that of Silver. ALOIS BILECKI (*Zeitsch. anorg. Chem.*, 1920, **110**, 341—344).—The atomic weight of barium (Ag = 107·88), 137·37, is practically identical with $447n_1 = 137{\cdot}38563$, where $n_1 = 0{\cdot}307350427$. When the atomic weight is found by analysis of the bromide, the value found is 0·011%, and by analysis of the chloride, 0·0403% low. E. H. R.

Radioactive Disintegration of the Atomic Nucleus. HANS TH. WOLFF (*Physikal. Zeitsch.*, 1920, **21**, 175—178).—A theoretical paper in which, accepting the hypothesis of Lindemann (A., 1915, ii, 720) that the instability of the atomic nucleus depends on a large number of particles which move independently inside the nucleus, and assuming that these particles follow Bohr's law in respect of the moment of impulse in their orbital motion, and that the velocity of the α-particle is the same within the nucleus as it is outside, a formula is deduced, from the Geiger-Nuttall relationship between the disintegration constant and the range of the α-particles and from the relationship between the velocity and range of the α-particles, whereby the disintegration constant is expressed as a function of the rotation number of the particles which are expelled as α-rays. A corresponding formula is developed from purely theoretical considerations, and an equation giving the conditions which must hold for both formulæ to be identical. The formulæ are applied to the case in which the motion, of the particles under consideration, undergoes no change during a single step in the disintegration of the atom. J. F. S.

Arrangement of Electrons in the Elements of the Long Periods. R. LADENBURG (*Naturwiss.*, 1919, **8**, 57; from *Chem. Zentr.*, 1920, i, 599—600).—In his previous communication (this vol., ii, 301), the author did not take into account certain definite results obtained by Baerwald in connexion with the irregularities in the atomic volume curve, since they were unknown to him at the time. H. W.

The Binuclear Atomic Theory and the Disintegration of Nitrogen. O. HINSBERG (*Chem. Zeit.*, 1920, **44**, 294).—The observation of Rutherford (A., 1919, ii, 260) that by bombardment with α-particles from radium-*C* the nitrogen atom is disintegrated, with the production of rapidly moving hydrogen particles, is in agreement with the author's theory that the elements of the fifth to the eighth groups of the periodic system possess two valency centres (A., 1919, ii, 505). Rutherford considers that the hydrogen nucleus which is separated from the nitrogen atom by the α-particle is situated relatively far from the principal nucleus of the nitrogen atom. In all probability, Rutherford's principal helium-containing nucleus in the nitrogen atom is identical with the author's postulated quadrivalent nucleus, whilst his hydrogen-containing nucleus corresponds with the author's univalent nucleus in the nitrogen atom. E. H. R.

Absolute Saturation of the Attractive Forces Acting between Atoms and Molecules. M. POLÁNYI (*Zeitsch. Elektrochem.*, 1920, **26**, 161—171).—A theoretical paper in which the absolute saturation of the attractive forces between atoms and molecules is considered. Absolute saturation is defined as follows: If an atom or molecule attracts a molecule AB from infinity with a force F_{AB}, and each of the atoms separately with forces F_A and F_B, respectively, then when $F_{AB} < F_A + F_B$, an absolute saturation of the forces F_A and F_B takes place in the formation of the molecule AB. A number of cases are cited to show that absolute saturation is of common occurrence, among which are included adsorption of gases. It is shown also that in a *non-additive field* of force, particularly in interatomic and intermolecular fields, which show absolute saturation, the heat of formation of the molecule changes with its position in the field, even when the field is homogeneous. Hence it follows that non-additive fields, which exhibit absolute saturation, can only be produced from hetero-polar systems. J. F. S.

Barger's Microscopical Method of Determining Molecular Weights. I. The Principle of the Method with Reference to the Molecular and Ionic Attraction of Solute for Solvent. KUMAO YAMAKAMI (*Biochem. J.*, 1920, **14**, 103—113).—It is proved that the force which effects the volume change in the drops is not simply the vapour pressure, but also the osmosis through the thin film of liquid between the drops. When the length of interval between the drops is 2—3 mm., as much as five-sixths or six-sevenths of the volume change is attributable to osmosis. It is therefore possible to measure molecular weights or the degree of association or dissociation by investigating the volume-change of drops which are brought in contact with drops of standard solutions of known molecular concentration. J. C. D.

Valve for Glass Apparatus. KURT BUNGE (*Chem. Zeit.*, 1920, **44**, 299).—The valve consists of a glass tube melted solid in one spot. On both sides of this are two small holes, not more than 10 mm. apart. A piece of coloured glass marks the position of the valve. A piece of rubber tubing is slipped over the valve, and the latter is operated by gentle pressure by the thumb and forefinger on the rubber. The valve may be used on burettes, or on pipettes to prevent liquid entering the mouth. J. R. P.

Effective Connecting Bulb. C. M. CLARK (*J. Ind. Eng. Chem.*, 1920, **12**, 366).—A bulb tube for preventing spray passing from a distillation flask into the receiver consists of a simple bulb on a tube, but the bulb has an internal baffle-plate in the form of a deep, inverted watch-glass; the latter is attached to the end of the upper tube (this end extends a short distance into the bulb), and the edge of the baffle-plate reaches to within 5 mm. of the side of the bulb. W. P. S.

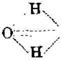
Manometer for Vacuum Distillation. H. T. CLARKE (*J. Amer. Chem. Soc.*, 1920, **42**, 786).—A manometer is described, for use in vacuum distillation, which is designed to prevent liquid passing into the exhausted limb and also to prevent breakage if air should suddenly enter the distillation apparatus. The modification consists in the introduction of a hook-shaped trap half-way up the evacuated limb. The trap consists of a very fine capillary tube widened at one end and sealed to the walls of the manometer tube. This effectually prevents moisture getting into the exhausted space, and if the pressure suddenly drops it prevents the mercury rushing in and breaking the top of the manometer tube. J. F. S.

A Device for Regulating the Temperature of Incubators either above or below Room Temperature. JOHN H. NORTHROP (*J. Gen. Physiol.*, 1920, **2**, 309—311).—The water flow through the jacket of a double-walled incubator is regulated by causing a relay to direct a stream of water either through the incubator or to waste as required by the temperature changes. This is brought about by means of a wire attached to the armature of the relay and attached at the other end to a glass pipette at the end of a vertical rubber tube. The current necessary to move this wire and pipette is so small that it is unnecessary to use a secondary circuit. The regulator may be either of the mercury–toluene or bimetallic type. J. C. D.

Inorganic Chemistry.

Generation of Hydrogen by the Reaction between Ferrosilicon and Sodium Hydroxide Solution. E. R. WEAVER (*J. Ind. Eng. Chem.*, 1920, **12**, 232—240).—The preparation of hydrogen from ferrosilicon, sodium hydroxide, and water is most economically effected by dissolving sodium hydroxide in water so as to form a 20—30% solution, mixing a portion of this solution and ferrosilicon in the reaction chamber, and when the temperature has reached 0° adding ferrosilicon and the remainder of the sodium hydroxide solution at a uniform rate in order to keep the temperature constant. About equal weights of ferrosilicon and sodium hydroxide may be used. Towards the end of the operation, the reaction mixture is cooled by means of an internal spray of water. W. P. S.

The Constitution of Hydrogen Peroxide. ANTONIO RIUS Y MIRÓ (*Helv. Chim. Acta*, 1920, **3**, 347—365).—The validity of Willstätter and Hauenstein's argument against the unsymmetrical formulæ for hydrogen peroxide (A., 1909, ii, 566), based on the reduction of benzoyl peroxide to benzoic acid as distinguished from

benzoic anhydride, is weakened by the fact that water formed in the reaction might hydrolyse any anhydride formed. The same result has now been obtained, however, by reduction in boiling benzene solution with yellow phosphorus. In addition, potassium orthophosphate is the sole product of the reduction of potassium perphosphate by potassium iodide in acetic acid solution, or by ferrous or cobalt hydroxides in alkaline solution. It is also shown that sulphuric acid cannot be oxidised to persulphuric acid by permanganic acid, plumbic salts, or nickel peroxide. The majority of oxidations due to hydrogen peroxide are really hydroxylations, but, although this is contrary to the asymmetrical formula, the case of potassium permanganate shows it does not necessarily lead to the symmetrical formula. This formula does not explain the reducing properties of hydrogen peroxide, which the author attributes to weakly-bound hydrogen atoms. By anodic oxidation of solutions of potassium hydroxide containing potassium fluoride, up to 5·35% of hydrogen peroxide, calculated on the energy expended, was obtained (compare Riesenfeld and Reinhold, A., 1909, ii, 879). The action of ozone on fuming sulphuric acid (Schmidlin and Massini, A., 1910, i, 498) and of perchromic acid on hydrogen peroxide were also examined, evidence of interaction being obtained in the latter case (compare Riesenfeld, A., 1909, ii, 51). The author suggests the formula  for hydrogen peroxide, and proposes that peroxides of the general type RO_2R be called anhydro-hydroperoxides, to distinguish them from Baeyer's hydroperoxides, RO_2H. As a test for hydroperoxides which can only be examined in acid solution, and to which Riesenfeld and Mair's test cannot therefore be applied (A., 1912, ii, 156), hydrogen peroxide itself is suggested. One molecule of oxygen is liberated, whilst the anhydroperoxides merely form an additive product. J. K.

Viscosity of Sulphur. C. COLERIDGE FARR and D. B. MACLEOD (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 80—98).—The viscosity of molten sulphur has been determined at a series of temperatures by the method of rotating cylinders. It is shown that the viscosity of twice distilled, but not gas-free, sulphur has the value 0·1094 *C.G.S.* units at 123°, and from this temperature it falls to a minimum of 0·0709 *C.G.S.* units at 150° and then rises to 0·0759 at 159°, when the rise becomes more marked, but nothing of the nature of a strict transition point is observed. Exposure to air in the molten condition, especially below 160°, has a marked effect on the viscosity from 160° upwards. The effect is a slow one, the viscosity continuing to rise for as much as forty-eight hours on exposure to the air for that time. The maximum for purified gas-free sulphur is reached at 200°, when the value is 215 *C.G.S.* units; the maximum for purified but not gas-free sulphur, after a long exposure to air, is reached at 190°, and has a value about 800 *C.G.S.* units. Crystallisation has an apparent, but probably

secondary, effect on the viscosity as measured at any temperatu It apparently raises the viscosity of a low-valued sample of sulph and lowers the viscosity of a high-valued sample. The effect crystallisation seems to disappear when the viscosity of the samp is about 300 *C.G.S.* units at 171°. Sulphuric acid appears to be t impurity which, after exposure to the air, causes the extreme vari tions which are found in the values of the viscosity of air-expos sulphur. Changes in the viscosity are accompanied by a cor sponding change in the amount of insoluble sulphur present.

J. F. S.

A New Hydrogen Sulphide Generator. BERTRAM DILL STEELE and HENRY GEORGE DENHAM (T., 1920, **117**, 527—529).

Solubility of Gases in Water. Sulphur Dioxide. FREI (*Chem. Zeit.*, 1920, **44**, 294).—Determinations of the solubility sulphur dioxide in water between 0° and 40° at 760 mm. ha been made, and the results are given in grams and in litres of g dissolved per litre of water. At 0° the solubility is 228·29, 10° 162·09, at 20° 112·90, at 25° 94·08, at 30° 78·67, and at 4 54·11 grams per litre.

E. H. R.

Catalytic Synthesis of Ammonia. M. GUICHARD, VAV CORNEC, CANTRAGREL, STEVENSON, APARD, and BOURDIOL (*Bu Soc. d'Encour.*, 1920, **132**, 71—102).—The authors have inves gated the catalytic manufacture of ammonia, especially as regar the suitability of various catalysts. Addition of magnesia alumina greatly increases the life of catalysts, such as iron, coba nickel, tungsten, and molybdenum, and a combination of two these metals ensures greater catalytic efficiency. Iron–molybden was proved to be the most resistant and to give the high ammonia concentration—more than 4%. Iron alone gave l than 1%, molybdenum less than 1·5%, nickel 3%, and cobalt 3 The best method of preparation is by precipitation of ferric nitra with ammonium molybdate, followed by ignition, and subseque reduction. With perfectly dry gases, uranium is a suita catalyst, but its combinations with cobalt and molybdenum a inferior. Uranium–nickel gives poor results, and uraniu tungsten is practically inert. The authors have made a part study of the whole cycle of operations, including the circulation the gases, the recovery of heat, absorption of ammonia unc pressure, and the most suitable arrangement of the furnace. [S further, *J. Soc. Chem. Ind.*, 1920, 362A.]

W. J. W.

Vapour Pressure of Ammonia. C. S. CRAGOE, C. H. MEYE and C. S. TAYLOR (*J. Amer. Chem. Soc.*, 1920, **42**, 206—229). The vapour pressure of ammonia has been determined over t temperature range −78° to +70° by the manometric metho Several forms of manometer are described in the paper. Sev different samples of ammonia were used in the experiments, a these contained less than 1 part per 100,000 parts of non-c

densing gas and less than 0·01% by weight of other impurities. The phenomenon of hysteresis was observed near the boiling point of ammonia with a commercial specimen which contained a small amount of air; this indicates the absolute necessity of very complete removal of dissolved gases for any accurate measurements of vapour pressure by the static method. The normal boiling point of ammonia was determined by both the static and the dynamic method, and the mean of the two results found to be $-33·35°$. Empirical equations are deduced which represent the vapour pressure over the measured range; the results of 122 measurements between $-78°$ and $+25°$ agree with the values calculated by means of these equations to within 1 millimetre, and the results of 28 measurements between $+25°$ and $+70°$, made with a calibrated piston gauge, agree to within 3 millimetres. The vapour pressure of ammonia is expressed between $-80°$ and $+70°$ by either of the equations $\log_{10}p = 30·256818 - 1914·9569/\theta - 8·4598324\log_{10}\theta + 2·39309\times10^{-3}\theta + 2·955214\times10^{-8}\theta^2$ or $\log_{10}p = 12·465400 - 1648·6068/\theta - 0·016386460\theta + 2·403276\times10^{-5}\theta^2 - 1·168708\times10^{-8}\theta^3$, where p is expressed in millimetres of mercury and θ in degrees absolute (abs. degrees = C° + 273·1). The slope of the vapour pressure–temperature curve is obtained by differentiation of either of the above equations. J. F. S.

Preparation of Mixtures of Nitrogen and Hydrogen by Decomposition of Ammonia. R. O. E. DAVIS and L. B. OLMSTEAD (*J. Ind. Eng. Chem.*, 1920, **12**, 316—317).—The catalytic *decomposition of ammonia* by heat in the presence of iron, first investigated by Ramsay and Young (T., 1884, **45**, 88), and subsequently by Perman and Atkinson (*Proc. Roy. Soc.*, 1905, **74**, 110), has been studied under manufacturing conditions, an electrically heated iron autoclave packed with iron turnings being used for the purpose. At 370°, 73% of the ammonia was decomposed, at 470° 84%, at 540° 94%, at 650° 99·6%, and at 735° 99·7%. In practice, about 100 cu. ft. per hour of the mixture of hydrogen and nitrogen could be obtained at 675° with a loss of 0·3 to 0·4% of ammonia. The equilibrium of a system H_2–N_2–NH_3 at that temperature corresponds with about 0·02% of ammonia. The average time of contact was about five seconds. When copper was used as the catalyst, a temperature about 200° higher and longer contact were required, which is in accordance with the facts observed by Beilby and Henderson (T., 1901, **79**, 1245). [See, further, *J. Soc. Chem. Ind.*, 1920, 362A.] C. A. M.

The Discoverer of Phosphorus. LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1917, **5**, 238—243).—In chemical literature, the discoverer of cobalt is sometimes mistaken for the discoverer of phosphorus, or at least their names are spelt in the same manner (Brandt). The German alchemist Brand (born 1625) discovered phosphorus in the year 1669, 1674, or 1677, whilst the discovery of cobalt was made (1733 or 1735) by the Swedish chemist Brandt (1694—1798) (compare A., 1919, ii, 511). W. R. S.

Preparation of Arsenic Trichloride from White Arsenic and Carbonyl Chloride. L. H. MILLIGAN, W. A. BAUDE, and H. G. BOYD (*J. Ind. Eng. Chem.*, 1920, **12**, 221—223).—When carbonyl chloride is passed over a mixture of arsenic trioxide (80%) and carbon (20%) heated at 200° to 260°, arsenic trichloride is formed, the yield being almost quantitative. The method has been used as a means of utilising the impure "tail gas" from carbonyl chloride manufacture. It is probable that the treatment of inorganic compounds with carbonyl chloride in the presence of carbon as a catalyst may be used as a general method of chlorination. W. P. S.

Reversible Oxidation of Arsenious Acid. C. MATIGNON and J. ALLAIN LECANU (*Compt. rend.*, 1920, **170**, 941—943).—When arsenious oxide is heated with oxygen at temperatures varying from 400° to 480° and pressures of 127—180 atmos., a certain amount of oxidation occurs, the extent of oxidation, other things being equal, increasing with the temperature. Similarly, a concentrated solution of arsenious oxide in aqueous sodium hydroxide at 80° under a pressure of oxygen equal to 50 atmos. is oxidised to the extent of 10·9% in five hours. W. G.

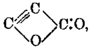
The Disposition of the Atoms and the Optical Rotation of Quartz and Sodium Chlorate. J. BECKENKAMP (*Zeitsch. anorg. Chem.*, 1920, **110**, 290—310).—The structures suggested by previous workers for quartz, for example, those of Söhncke and Bragg, do not account for optical rotation in directions perpendicular to the principal axis. In the structure now proposed, the silicon atoms form a rhombohedral lattice instead of a three-point screw system, as in Bragg's structure. The spiral structure only appears after the introduction of the oxygen atoms, when the total structure is seen to be composed of nine three-sided, prismatic lattices. The disposition of the oxygen atoms is such that the orientation of the valency directions is the same in horizontal or vertical molecular layers, and the optical rotation perpendicular to the vertical axis is then accounted for. The different kinds of twin crystals of quartz, and the relation of quartz to tridymite, β-quartz, and crystoballite, are discussed. Sodium chlorate has a structure similar to that ascribed by Bragg to calcite, the calcium atoms being replaced by sodium and the carbon by chlorine.

E. H. R.

Luminous Carbon Flames Regarded as Turbid Media. HERMANN SENFTLEBEN and ELISABETH BENEDICT (*Kolloid Zeitsch.*, 1920, **26**, 97—100).—When an intense beam of light from an arc is projected on to a Hefner candle flame, the beam is bent from its original path and polarised. The authors have measured the amount of deflexion, the polarisation, and the intensity of the deflected beam. It is shown that the intensity of the deflected light varies strongly with the direction, in the sense that with increasing angle between the incident beam and the direction of

measurement it increases, for example, a change in the angle from 45° to 140° changes the intensity 300%. The fraction of the light which is polarised reaches a very definite maximum when the angle of observation is 90° to the incident light. At this angle, the fraction is 86%. The intensity of the deflected beam increases with decreasing wave-length; thus there is an increase in intensity of 150% as the wave-length changes from 0·700 μ to 0·475 μ. The experiments show that the carbon flame behaves in a manner analogous to that of a turbid medium. J. F. S.

Removal of Carbon Monoxide from Air. ARTHUR B. LAMB, WILLIAM C. BRAY, and J. C. W. FRAZER (*J. Ind. Eng. Chem.*, 1920, 12, 213—221).—Of various absorbents and catalytic oxidising substances examined, a mixture of MnO_2, 50%; CuO, 30%; Co_2O_3, 15%; and Ag_2O, 5%, gave the best results. The silver oxide was precipitated in the moist mixture of the other oxides, the mass then dried and ground to size. This mixture acts indefinitely at the ordinary temperature against any concentration of carbon monoxide in air, provided that the air is dry. When used in gas-mask canisters, the latter must be provided with a calcium chloride drying chamber at the inlet, and the "life" of the canister is then limited solely by that of the drier. W. P. S.

Constitution of Carbon Sub-oxide. H. STANLEY REDGROVE (*Chem. News*, 1920, **120**, 209—210).—By means of a method of calculation due to the author, the following theoretical numbers are found: for O:C:C:C:O, mol. heat of combustion, 243·6 Cal.; mol. heat of formation, 47·4 Cal.; for , mol. heat of combustion, 286·1 Cal.; mol. heat of formation, 4·8 Cal. A determination of the thermochemical data would enable the constitution of the compound to be settled. J. R. P.

Carbonyl Chloride. III. Action of Carbonyl Chloride on Industrial Iron Containers. M. DELÉPINE and L. VILLE (*Bull. Soc. chim.*, 1920, [iv], **27**, 288—290).—When it contains a little free chlorine, carbonyl chloride slowly attacks iron, and the resulting ferric chloride colours the carbonyl chloride yellow. The oxychloride free from chlorine will dissolve rust or the sub-carbonate of iron, and it is probably from this source that the ferric chloride in commercial carbonyl chloride comes. W. G.

Phase Diagram of Potassium and Sodium Chlorides and their Etched Figures. G. TAMMANN (*Nachr. Ges. Wiss. Göttingen*, 1919, 422—427; from *Chem. Zentr.*, 1920, i, 604).—Potassium and sodium chlorides form a continuous series of mixed crystals between 660° and 500°. Since neither salt has a transition point, the phenomena observed when the mixed crystals are cooled must be attributed to separation of the components. With diminishing temperature, therefore, either the attractive forces within

the molecules of the respective chlorides must increase, or those between the unlike molecules must be greatly weakened. The results obtained by etching the individual crystals at the ordinary temperature indicate that the intra-molecular forces of the potassium chloride crystal differ from those of the sodium chloride crystal, or, more precisely, that certain lattice regions are more closely united in the former, whilst such differences are not observed in the latter. In the light of these observations, it is surprising that Röntgen analysis indicates the same lattice for each crystal. A possible explanation of the etched figures, based on atomic lattice structure, is discussed. H. W.

Preparation of Sodium Amalgam in Flakes. ARTHUR D. HIRSCHFELDER and MERRILL C. HART (*J. Ind. Eng. Chem.*, 1920, **12**, 499).—To obtain sodium amalgam in readily pulverisable form the hot liquid amalgam is slowly poured into a vessel in which xylene or petroleum is mechanically agitated. The resulting flocculent deposit is dried on porous porcelain in a current of air. C. A. M.

The Variations in the Composition of Ammonium Phosphomolybdate. S. POSTERNAK (*Compt. rend.*, 1920, **170**, 930—933). —Ammonium phosphomolybdate precipitated from phosphate solutions in the absence of ammonium salts always contains phosphorus and molybdic oxide in a constant ratio. It consists of a variable mixture of di- and tri-ammonium phosphomolybdates, varying according to the composition of the ammonium molybdate solution used.

In the presence of 5% or more of ammonium nitrate or sulphate the phosphomolybdate precipitate obtained is a complex mixture of the types $16(NH_4)_3(MoO_3)_{12}PO_4,NH_4(MoO_3)_4NO_3$ and

$$8(NH_4)_3(MoO_4)_{12}PO_4,(NH_4)_2(MoO_3)_8SO_4$$

respectively. In all cases the molybdic acid behaves as though, in acid medium, it existed in the tetramolybdic state, and in this form combined with the hydroxyl groups of all the mineral acids present. This supports Kehrmann's view as to the constitution of phosphomolybdic acid (compare A., 1887, 777). W. G.

Formation of the Double Salts of Calcium and Potassium Sulphates at 100°. EVALD ANDERSON and R. J. NESTELL (*J. Ind. Eng. Chem.*, 1920, **12**, 243—246).—In determining the conditions of equilibrium for the formation of syngenite ($K_2SO_4,CaSO_4,H_2O$) and potassium pentacalcium sulphate at 100°, known weights of potassium sulphate and gypsum were shaken seven to twenty-three days with water in bottles immersed in boiling water, the resulting solutions rapidly filtered, and the potassium and calcium oxides and sulphuric anhydride estimated. Experiments were also made with previously prepared syngenite and potassium pentacalcium sulphate. The mean results showed that for the formation of the latter salt as in the equation $5(CaSO_4,2H_2O)+K_2SO_4 \rightleftharpoons K_2SO_4,5CaSO_4,H_2O+9H_2O$, the equilibrium concentration for

›tassium sulphate was 1·05 mols., and for the calcium sulphate 24 mol., per 1000 mols. of water. For the formation of the ıngenite,

$$K_2SO_4,5CaSO_4,H_2O + 4K_2SO_4 + 4H_2O \rightleftharpoons 5(K_2SO_4,CaSO_4,H_2O),$$

e equilibrium concentrations were 9·26 mols. of potassium lphate and 0·142 mol. of calcium sulphate per 1000 mols. of ater at 100°. These figures are considerably lower than those ›tained by extrapolation from the results of D'Ans at 83°. Hence e value given by D'Ans for potassium sulphate is too high, or e equilibrium curve has a maximum between 83° and 100°.

C. A. M.

Calcium Arsenates. I. Equilibrium in the System rsenic Oxide, Calcium Oxide, Water at 35° (Acid ›ction). C. M. SMITH (*J. Amer. Chem. Soc.*, 1920, **42**, 259—265) The equilibrium conditions between arsenic oxide, calcium oxide, d water have been determined at 35° for those mixtures in ıich the arsenic oxide is in excess and from which acid arsenates e likely to be produced. The results are recorded in a diagram represent the phase rule relationships. Two compounds are ınd to be stable under the experimental conditions, dicalcium thoarsenate monohydrate, $CaHAsO_4,H_2O$, which is identical with e mineral haidingerite, and monocalcium orthoarsenate. $H_4(AsO_4)_2$, which exist below and above, respectively, an acid ncentration corresponding with 27·5% of arsenic oxide.

J. F. S.

Atomic Weight of Radio-lead. R. DE MONTESSUS DE BALLORE ev. *gen. Sci. pure et appl.*, 1919, **30**, 673; from *Chem. Zentr.*, 20, i, 558).—The figure 206 has been proposed for this atomic ight; a much more probable value is 206·5 ± 0·05. H. W.

Micrometallurgy. ST. BOGDAN (*Bul. Soc. Chim. România*, 19, **1**, 60—72).—A micrographic study of the alloys of copper d silicon and iron and silicon. In all such alloys, when the rcentage of silicon is very small, the result is a homogeneous id solution. If the amount of silicon present exceeds 1%, stalline compounds, embedded in the solid solution of the alloy, always obtained, and are probably silicides. When the silicon ıtent exceeds 4%, two crystalline silicides can be isolated, and o silicon in a crystalline and in an amorphous state. Prolonged ıting of the alloys at high temperatures facilitates the separ-on of their components. As the proportion of silicon present reases further, the mass becomes more crystalline, the hardness reasing, the alloy becoming more friable. W. G.

Copper-Aluminium-Zinc Alloys of High Zinc Content. H. SCHULZ and M. WAEHLERT (*Metall. und Erz*, 1919, **16**,)—176, 195—201).—The thermal, structural, and mechanical operties of copper-aluminium-zinc alloys containing up to 10%

of copper and 10% of aluminium were investigated. Five sections of the three-dimensional equilibrium diagram are given, representing, respectively, alloys containing 2%, 4%, 6%, 8%, and 10% of copper with a varying aluminium content. A reproduction of the complete space diagram is also given, the principal features of which are two broad, curved surfaces intersecting in a eutectic line at 375°, running approximately parallel to the copper co-ordinate, and a second line, corresponding with 1·9% of copper, parallel to the aluminium co-ordinate, dividing the diagram into two unequal sections. The microscopic structure of the alloys confirms the conclusions drawn from their thermal study. Alloys containing less than 1·9% of copper and less than 0·75% of aluminium consist of homogeneous ternary mixed crystals. Those with more than 1·9% of copper and up to 0·8% of aluminium consist of a solid solution of ϵ-crystals of the zinc–copper series with α-aluminium crystals. The remainder of the alloys fall into five groups, according to the thermal equilibrium diagram, but only four of these can be distinguished by their structure.

The mechanical properties studied were the hardness, tensile strength, and crushing strength. No relation could be found between the tensile strength and the equilibrium diagram. The curves of equal hardness and of equal crushing strength, however, show an inflexion at a point which appears to correspond with the limit of solubility of zinc crystals in the alloys. E. H. R.

Mechanism of the Formation and the Properties of Mercury Hydrosols prepared by Various Methods of Dispersion. IVAR NORDLUND (*Kolloid Zeitsch.*, 1920, 26, 121—138).—Methods of preparing mercury sols by various methods are described. The methods are subdivided into three groups. (i) mechanical dispersion, (ii) thermal dispersion, and (iii) electrical dispersion. Mercury sols of small stability are produced when a fine stream of mercury is allowed to fall into a solution of potassium citrate ($0·5-5\times10^{-3}N$) or a solution of gelatin (0·1%) with a velocity of 100 metres per second. In the latter case, a black coagulum is obtained, which consists of highly dispersed mercury and gelatin, and is readily peptised by warming with a trace of alkali to form a grey sol. Shaking mercury with conductivity water produces a very little of a rapidly sedimenting sol; the addition of potassium chloride, sodium chloride, potassium nitrate, potassium sulphate, copper sulphate, mercurous nitrate, and acetic acid to the water did not increase the sol formation. The presence of ammonia ($1\times10^{-3}N$) in the water produced a sol which was not very stable, complete sedimentation occurring in two or three days. Ammonium chloride and sulphate solutions shaken with mercury produced sols which, in the case of ammonium chloride, were much more stable than in any of the previous cases. Shaking with a solution of potassium citrate ($2-7\times10^{-3}N$) produced a very concentrated sol, which was coagulated by higher concentrations of citrate. This sol has a strong reddish-brown-grey colour, and is very stable. It may be kept for months without

oagulating. Shaking with solutions of carbamide (0·01%) and gelatin (0·0001—0·0025%) produced a dilute, grey sol. The formation of sols by the "spirting" method is held to be due to a spontaneous atomising of the rushing mercury stream and to the atomising of the larger drops against the walls of the vessel. In he shaking experiments, the formation of sols is due to the disintegration of thin laminæ of mercury; the bursting of mercury bubbles has little effect in sol formation. A deep brown, very concentrated sol was formed by distilling mercury from a porcelain etort through a red-hot silica tube, and thence through a fine jet nto cold water. The mercury vapour entered the water with a elocity of 160 metres per second. The sol is not very stable, and n ten to fifteen minutes it had lost its brown colour, and in two r three days it had completely and irreversibly coagulated. Experiments, of the type often described, by electrical dispersion, oth with direct and alternating current arcs, are also described. The partition of the radii of the particles has been worked out for he more stable of the sols described. J. F. S.

Compounds of Oxides. (Mlle) S. Veil (*Compt. rend.*, 1920, **70**, 939—941).—Mixtures of ceric and chromic oxides in different molecular proportions were compressed and heated by methods milar to those used for alloys. The electrical conductivity at igh temperatures and the coefficients of magnetisation at the rdinary temperature were then determined in each case. The urves showing the results indicate the existence of the compounds eO_2,Cr_2O_3, $3CeO_2,4Cr_2O_3$, $CeO_2,2Cr_2O_3$, and $CeO_2,5Cr_2O_3$, and the robable existence of the compounds $5CeO_2,Cr_2O_3$, $7CeO_2,4Cr_2O_3$, nd $CeO_2,9Cr_2O_3$. W. G.

The Reaction between Hydrochloric Acid and Potassium ermanganate. F. P. Venable and D. H. Jackson (*J. Amer. hem. Soc.*, 1920, **42**, 237—239).—It is shown that the reaction etween potassium permanganate and hydrochloric acid and hydroomic acid, respectively, takes place in two stages, which may, by gulating the quantity of acid employed, be separated. The action is represented: (i) $2KMnO_4 + 8HCl = 2KCl + 2MnO_2 + H_2O + 3Cl_2$; (ii) $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$. It is also own that hydrobromic acid reacts at a concentration $0·00154N$, hilst with hydrochloric acid no reaction takes place until the ncentration reaches $0·002N$. J. F. S.

System Hydrated Ferric Oxide–Arsenious Acid. Wilhelm ltz (*Kolloid. Zeitsch.*, 1920, **26**, 179—180).—A criticism of yng's paper (A., 1918, ii, 317) on the adsorption compounds of ric arsenite. Compare also Biltz and Utescher (A., 1905, ii, 807). J. F. S.

Influence of Superimposed Alternating Current on the nodic Formation of Ferrates. G. Grube and H. Gmelin eitsch. Elektrochem., 1920, **26**, 153—161).—An investigation of

conditions under which sodium ferrate is formed by anodic oxi tion in concentrated sodium hydroxide. It is shown that incre ing temperature and alkali concentration favour large yiel With increasing current density the yield increases to maximum, and then falls with any further increase in the curr density. The current yield of sodium ferrate can be consideral increased by superimposing an alternating current over the dir current. The increase in the yield, for constant direct curre reaches a maximum for a definite alternating current density. Usi as electrolyte 40% sodium hydroxide with an iron anode and platinum cathode and electrolysing at 35° with a direct current 3·33 amps./sq. dcm. and an alternating current of 5·0 amps./ dcm., an increase of 160% in the yield of sodium ferrate is obtain In the preparation of concentrated solutions of ferrates the anc and cathode must be separated, and since ferrates lose oxygen 50° and precipitate ferric hydroxide, this temperature must not exceeded in the preparation, and the velocity of formation must increased by imposing an alternating current on the direct curre In this way undecomposed saturated solutions and the crystall salts may be obtained. J. F. S

The Nature of Subsidiary Valencies. XXIV. Salts wi High Ammonia Content. Fritz Ephraim and Franz Mo (*Ber.*, 1920, **53**, [*B*], 548—563).—Recently, the addition of a monia to salts containing a particularly large anion united tc small cation has been investigated, and it has been shown tl ammines with unusually high ammonia content are thereby form (A., 1918, i, 389). In the previous communication, salts of orga acids were employed, but it is now shown that suitable inorga complexes behave in a similar manner, and ammines of the ac

$$H\left[Co\begin{matrix}(NO_2)_4\\(NH_3)_2\end{matrix}\right],\ H\left[\begin{matrix}C_2O_4\\Co(NO_2)_2\\(NH_3)_2\end{matrix}\right],\ H\left[Cr\begin{matrix}(CNS)_4\\(NH_3)_2\end{matrix}\right]\ \text{and}\ H[I(As_2O_4)$$

are now described. Addition of ammonia proceeds in many ca beyond the octammine stage, and, in extreme cases, leads to liquefaction of the salts. The colour of the highly ammoniated co pounds does not differ markedly from that of the hexammines, the volume does not greatly increase when ammonia is added bey the hexammine stage, whilst, also, reaction occurs without any gr development of heat. The higher ammines do not exhibit a s wise degradation to lower ammines with rise of temperature, l generally speaking, gradually evolve ammonia in much the sa manner as does a solid solution or adsorption compound.

The author extends his previous theory (*loc. cit.*) on the influe of the relative size of anion and cation on the properties of the s The presence of neutral portions (water, etc.) is supposed in manner to fill the seams of the crystal caused by the unequal pai of anion and cation, and thus to stabilise the whole structure. Ac tion of water as "packing material" increases the likeness of

t to water, and hence the solubility in water. The most sparingly uble salts are therefore to be expected among such as contain st equally matched anion and cation; in general, the cation is itially greater than the anion, the largest of the latter being resented by the alkali metals, particularly cæsium; with volumin- ; anions (perchlorate, platinichloride, etc.) it is precisely this tal which forms the relatively least soluble salts, whilst the corre- nding salts of other metals only crystallise after enlargement of cation by the addition of neutral substances. Conversely, bulky ic radicles are best precipitated by acid radicles of compact ucture (ClO_4, $PtCl_6$, picric acid), quite apart from any question basic character.

The following individual salts are described which, in general, are pared by *mixing suitable components in the presence of* monia:

Tetranitritodiamminocobalti-compounds, $[Co(NO_2)_4(NH_3)_2]_2M$.— ckel: *hexammine* and *octammine*. Copper: *tetrammine* ($+H_2O$), e-green, microscopic prisms, and *octammine*. Zinc: *pentammine* l (?) *hexammine*.

Oxalodinitritodiamminocobalti-compounds.—Nickel: *octammine*, ble at the ordinary temperature; *decammine*, formed at $-13°$, l, possibly, *dodecammine* at still lower temperature. Copper: *rammine*, red needles, which did not further absorb ammonia at 8°. Zinc: *tetrammine*, *hexammine*, and *octammine*. Cadmium: *rammine*, pale red crystals which do not absorb ammonia.

Tetrathiocyanatodiamminochromi-compounds.—Nickel: *tetram- ie*, which passes into the *nonammine* at the ordinary temperature l becomes completely liquefied when treated with ammonia at 0°. Copper: (?) *tetrammine* and *octammine*. Cadmium: *dec- mine*, which becomes partly liquid when treated with excess of monia at $-20°$. Zinc: *monammine*, *octammine*.

Compounds derived from $H[I(As_2O_3)]$ (compare Weinland and ahl, A., 1919, ii, 411).—Zinc: *heptammine*, which passes through eries of solid solutions to the *hexammine* (at 70°), which is con- ted to the *tetrammine* (at 87°); the latter is stable up to 200°, at 210° passes into the *diammine*. Nickel: one molecule of salt nbines with the following numbers of molecules of ammonia: 1 at $-20°$; 14·2 at $+18°$; 10·3 at 66°; 1·2 at 77°.

Attempts to obtain disulphitotetramminocobalti-, heptanitroso- phonicferri-, and dinitrosothiosulphatoferri-salts of the heavy tals were unsuccessful. Salts such as copper metachloroantimon- are decomposed by ammonia into their components, which then arately absorb the gas. H. W.

Reversible Reactions of Water on Tungsten and its ides. GEORGES CHAUDRON (*Compt. rend.*, 1920, **170**, 1056—1058).

At 850° the two reversible reactions may be expressed by $+2H_2O \rightleftharpoons WO_2+2H_2+L_{850}$ and $2WO_2+H_2O \rightleftharpoons W_2O_5+$ $+L_{850}$. The value of L_{850} for the first reaction is $2\times4·4$ Cal., l for the second 4 Cal. W. G.

Solubility in the Solid State of Tin in Lead. N. PARRAVANO and A. SCORTECCI (*Gazzetta*, 1920, **50**, i, 83—92).—In view of the discordance between the values given by different investigators for the solubility of tin in lead in the solid state (compare Rosenhain and Tucker, A., 1908, ii, 1038; Degens, A., 1909, ii, 888; Mazzotto, A., 1911 ii, 889; Parravano and Sirovich, A., 1912, ii, 846; Guertler, *Metallographie*, 736, and *Zeitsch. anorg. Chem.*, 1916, **98**, 97) the authors have measured the electrical conductivities of a series of nineteen tin–lead alloys at various temperatures lying between that of the air and that of the eutectic alloy.

The conductivity isotherms are found to consist of two branches, that in the neighbourhood of the lead axis indicating the existence of solid solutions. The limits of miscibility in the solid state of tin in lead, corresponding with the points of intersection of the two branches, show that the percentages of tin in the saturated solutions at different temperatures are as follows: 14·5 at 175°; 13·5 at 170°; 12·5 at 162°; 10 at 150°; 6·5 at 100°; 5·0 at 75°; 3·0 at 50°; and 1·5 at 25°. These values differ considerably from those given by Rosenhain and Tucker and from those assumed by Guertler, the first three of them being in moderately good agreement with Mazzotto's figures.

The curve along which tin separates from its solid solntions in lead at temperatures below the eutectic temperature is very regular and confirms the conclusion that the recalescence observed with the solid alloys is due to a simple supersaturation phenomenon.

T. H. P.

Colloidal Rhodium. C. ZENGHELIS and B. PAPACONSTANTINOU (*Compt. rend.*, 1920, **170**, 1058—1061).—Colloidal rhodium may best be prepared by the following process. The metallic rhodium after suitable purification, is converted into the double chloride $Na_6Rh_2Cl_{12}$. This is dissolved in water, and to the slightly alkaline solution a solution of sodium protalbate is added and then a suitable reducing agent. Of the reducing agents tried, formaldehyde at 40° in a slightly alkaline solution is the most satisfactory, and under these conditions a clear, colloidal solution of rhodium is obtained. On purification by dialysis and subsequent evaporation to dryness in a vacuum, ebony-black plates are obtained which contain 33% of rhodium.

The colloidal solution of rhodium absorbs hydrogen to the extent of 2510—2960 times the volume of rhodium present. Similarly, the rhodium absorbs 346 times its volume of carbon monoxide at 12—14° and 1820 times its volume at 60°. The colloidal solution slightly alkaline, causes a very slight combination of nitrogen and hydrogen to give ammonia, the reaction being considerahly enhanced if the solution is made just acid with very dilute tartaric acid in the presence of potassium tartrate.

W. G.

Mineralogical Chemistry.

Colouring Matters of Red and Blue Fluorite. CECIL STEVENSON GARNETT (T., 1920, **117**, 620—622).

Aphthitalite (= Glaserite) from Searles Lake, California. W. F. FOSHAG (*Amer. J. Sci.*, 1920, [iv], **49**, 367—368).—Colourless, tabular, rhombohedral crystals were found embedded in powdery borax in a well boring at this locality. Material collected for analysis showed under the microscope some admixed halite. The following figures correspond with K_2SO_4, 72·37; Na_2SO_4, 18·38; NaCl, 7·87%, or $K_2SO_4 : Na_2SO_4$ about 4 : 1.

K.	Na.	SO_4.	Cl.	H_2O.	Total.
32·46	9·01	53·71	4·76	0·10	100·04

L. J. S.

Analytical Chemistry.

Substitutes for Platinum Wire for Flame and Bead Tests. C. C. KIPLINGER (*J. Ind. Eng. Chem.*, 1920, **12**, 500).—Borax beads may be made by heating the "lead" from a blacklead pencil to redness, dipping it into borax, and again placing it in the flame, so that a drop of the melted substance is suspended from the end. In using a roll of filter paper instead of platinum wire for flame tests (Ehringhaus, this vol., ii, 263), a flame of longer duration is produced, by introducing the rolled slip into a glass tube, with constricted opening, containing the solution or the substance moistened with hydrochloric acid. About 3 cm. of the paper is allowed to project, and the tube is inclined so as to feed the wick thus formed. C. A. M.

Thioacetic Acid as a Reagent. NAZARIO ALVAREZ (*Bol. minero soc. nac. min. Chile*, 1919, **31**, 181—191).—Finely powdered phosphorus pentasulphide (300 grams) and glacial acetic acid (300 grams) are mixed in a 2-litre flask containing glass beads (150 grams) to prevent ignition, and the mixture is carefully heated to a temperature not exceeding 100°; thioacetic acid begins to distil at 91°. Redistillation of the liquid serves to remove traces of arsenic and antimony. The ammonium salt is obtained by adding a slight excess of 10% ammonia to 10 c.c. of thioacetic acid. By diluting this solution to 30 c.c. a 33% solution of ammonium thioacetate is obtained, which, used in acid solution at 80—90°, has advantages (control of quantity, temperature, etc.) over hydrogen

sulphide for the precipitation of the bases of group II as sulphides; the filtrate, which contains ammonium chloride, is rendered available for the next group by boiling to remove hydrogen sulphide. The solution of ammonium thioacetate is not stable, and should be prepared when required for immediate use.

CHEMICAL ABSTRACTS.

Device for Preventing Over-titration. R. ORTHNER (*Chem. Zeit.*, 1920, **44**, 282—283).—A tube of about 5 mm. internal diameter, open at the top and constricted to a moderately fine jet at the lower end, is suspended vertically in the beaker containing the solution to be titrated; a short bent side-arm near the top of the tube is hooked over the edge of the beaker to keep the tube in position. The portion of the solution contained in this tube is not acted on by the reagent during the titration; the main portion of the solution is titrated until a very slight excess of reagent has been added; the tube is then raised so that its contents mix with the main portion of the solution, and the titration is completed.

W. P. S.

Colorimetric Determination of Titration Curves. LOUIS J. GILLESPIE (*J. Amer. Chem. Soc.*, 1920, **42**, 742—748).—A simple method is described for obtaining titration curves colorimetrically. The hydrogen ion exponents are determined without the use of buffer mixtures. Instead of a buffer mixture containing the indicator, a colour standard is used, consisting of a pair of test-tubes containing together 10 drops of indicator solution of suitable strength, the drop ratio in the two tubes being varied from 1:9 to 9:1. One tube of the pair contains dilute alkali and the other contains dilute acid. Reference to a table gives the hydrogen ion exponent corresponding with the drop ratio, or the exponent can be calculated from the relation $P_H = k + \log$ (drop ratio), where the drop ratio is the ratio of the number of drops of the indicator solution in the alkali tube to that in the acid tube, and k is a constant depending on the indicator. It has the following values for the indicators named: tetrabromophenolsulphonephthalein, 4·1; methyl-red, 5·0; dibromo-*o*-cresolsulphonephthalein, 6·3; dibromothymolsulphonephthalein, 7·1; phenolsulphonephthalein, 7·7; *o*-cresolsulphonephthalein, 8·1; and thymolsulphonephthalein, 8·8.

J. F. S.

Potassium Hydrogen Phthalate as a Standard in Volumetric Analysis. W. S. HENDRIXSON (*J. Amer. Chem. Soc.*, 1920, **42**, 724—727. Compare A., 1915, ii, 797).—Potassium hydrogen phthalate is shown to be an excellent standard for volumetric work. It is best prepared from phthalic anhydride and potassium carbonate, and is obtained absolutely pure by three crystallisations. It contains no water of crystallisation, and is not hygroscopic, so that weighings may be made in open vessels. Its solubility has been determined in water, and the following values

obtained: 25°, 10·23%; 35°, 12·67%; and at the boiling-point of the saturated solution, 36·12%. J. F. S.

Automatic Methods of Gas Analysis depending on Thermal Conductivity. E. R. Weaver, P. E. Palmer, H. W. Frantz, P. G. Ledig, and S. F. Pickering (*J. Ind. Eng. Chem.*, 1920, **12**, 359—366).—An apparatus is described for the continuous analysis of gas mixtures by an electrical method depending on the thermal conductivity of the gas as compared with that of a standard gas or mixture. The apparatus is given in detail, and it may be adapted to record results automatically. W. P. S.

New Forms of Combustion Apparatus for Use in Gas Analysis. E. R. Weaver and P. G. Ledig (*J. Ind. Eng. Chem.*, 1920, **12**, 368—370).—A combustion pipette, of about 150 c.c. capacity, is provided with two short side-tubes, the outer ends of which are fitted with glass caps. These caps are cemented on and have short platinum leads passing through them, the inner ends of the leads connecting with a platinum spiral extending across the pipette from one side-tube to the other. A combustion capillary is also described; the igniting spiral of platinum wire extends vertically down a portion of the capillary between two short side-arms fitted with caps carrying the leads. This portion of the capillary is surrounded by a small water-jacket. W. P. S.

Estimation of Chlorine with the Nephelometer. Arthur B. Lamb, Paul W. Carleton, and W. B. Meldrum (*J. Amer. Chem. Soc.*, 1920, **42**, 251—259).—The conditions to be observed in estimating traces of chlorine in alcohol and acetic acid solutions, by means of the nephelometer, have been investigated. It is shown that in a 50% alcohol water solution, heating silver chloride suspensions of widely differing concentrations at 40° for thirty minutes after precipitation produces a more intense and constant opalescence than can be attained at ordinary temperatures; further heating for thirty minutes at 40°, or keeping at the ordinary temperature for an hour, produces no perceptible change in this opalescence. Using this treatment, chlorides in such solutions may be estimated with an average deviation of 3—4% over concentrations ranging between 4 and 300×10^{-6} *N*. Opalescence in such solutions decays more rapidly in diffuse daylight than in the dark. The opalescence of the same quantity of silver chloride in water is about 15% greater than in 50% alcohol or in 50% acetic acid.

J. F. S.

Carbonyl Chloride. I. Detection and Estimation of Free Chlorine in Carbonyl Chloride. Marcel Delépine (*Bull. Soc. chim.*, 1920, [iv], **27**, 283—286).—For the detection and estimation of free chlorine in carbonyl chloride by means of potassium iodide solution the concentration of the latter must not exceed 1%. After leading a known weight of the vapour of the carbonyl chloride into the potassium iodide solution, the free iodine is

titrated by means of standard thiosulphate. If the concentration of the potassium iodide solution exceeds 0·1% there is a risk of interaction between the iodide and the oxychloride with consequent liberation of iodine. W. G.

Carbonyl Chloride. II. Destruction of Carbonyl Chloride by Water; Estimation of Escaped Gases. M. Delépine, R. Douris, and L. Ville (*Bull. Soc. chim.*, 1920, [iv], **27**, 286—288).—Carbonyl chloride is only slowly decomposed by moisture in the air, but is rapidly decomposed by water, although in the latter case the presence of hydrochloric acid considerably retards the decomposition. For the estimation of traces of carbonyl chloride in the air, a known volume of the air is bubbled through 10 c.c. of a solution containing 1 c.c. of *N*-sodium hydroxide and 5 c.c. of 95% alcohol, the volume being made up with water. The liquid is then evaporated to 2 c.c. on a water-bath, 2 drops of acetic acid are added, and the whole is evaporated to dryness; the residue is taken up with 2 c.c. of water, again evaporated to dryness, and once more taken up with 2 c.c. of water and the chloride present titrated with *N*/40-silver nitrate. By this means it is possible to estimate the chlorine to 0·00005 gram. W. G.

Carbonyl Chloride. V. Estimation of Hydrogen Chloride in Carbonyl Chloride. M. Delépine, M. Monnot, H. Duval, and J. Lafore (*Bull. Soc. chim.*, 1920, [iv], **27**, 292—295).—Five grams of finely powdered dry mercury cyanide are placed in a perfectly dry flask fitted with a ground-in stopper carrying two tubes. The carbonyl chloride is introduced into the flask in a sealed bulb, and the flask is exhausted. The bulb is then broken, and after twelve to fourteen hours the hydrogen cyanide formed by the action of any hydrogen chloride in the carbouyl chloride on the mercury cyanide is aspirated off and collected in 50 c.c. of 2*N*-sodium hydroxide, and is then estimated by Denigès's method. W. G.

Some Factors influencing the Estimation of Chlorides in Soil. C. T. Hirst and J. E. Greaves (*Soil Sci.*, 1920, 9, 41—51).—For the estimation of chlorides in soil the Volhard method gives more concordant and, as judged by the gravimetric method, more nearly exact results than the Mohr method. The following is the most satisfactory procedure to adopt. One hundred grams of finely powdered soil are shaken for five minutes with 500 c.c. of water and the solution is clarified either by the addition of 2 grams of alum or by filtration through a Pasteur-Chamberland filter. Twenty c.c. portions of the clear filtrate are transferred to stoppered bottles, and an excess of *N*/10-silver nitrate is added, followed by 10 c.c. of 95% alcohol. The mixture is shaken until the silver chloride is coagulated, after which 2 c.c. of a 4% ferric sulphate solution and 5 c.c. of dilute nitric acid are added, and the excess of silver nitrate is titrated with *N*/10-ammonium thiocyanate. W. G.

Estimation of Iodide and Bromide in Mineral Waters and Brines. W. F. BAUGHMAN and W. W. SKINNER (*J. Ind. Eng. Chem.*, 1920, **12**, 358).—Iodides are estimated by the permanganate method (A., 1919, ii, 349). Another portion of the sample is distilled with ferric sulphate to remove iodine, the distillation then treated with a slight excess of ammonia, boiled, filtered, the filtrate evaporated to dryness, and the bromine estimated in this residue by the chromic acid method (this vol., ii, 48). W. P. S.

Detection of Sulphuric Ions Masked in Complex Compounds. P. JOB and G. URBAIN (*Compt. rend.*, 1920, **170**, 843—845).—The SO_4'' ion masked in complex cobalt compounds may be estimated by difference. The total SO_4'' is estimated in the ordinary way as barium sulphate, and the free SO_4'' is estimated by precipitation in the cold as benzidine sulphate. The difference between the two results gives the percentage of masked SO_4'' ions in the complex. W. G.

Differentiation of Masked and Apparent Sulphuric Radicles in Complex Salts. ANDRÉ KLING and DANIEL FLORENTIN (*Compt. rend.*, 1920, **170**, 993—995. Compare A., 1914, ii, 661).—A claim for priority over Job and Urbain (compare preceding abstract) for the use of benzidine hydrochloride in the estimation of free sulphate ions in complex cobalt salts. W. G.

Solubility of Benzidine Sulphate in Water. C. S. BISSON and A. W. CHRISTIE (*J. Ind. Eng. Chem.*, 1920, **12**, 485—486).—The solubility of benzidine sulphate in water at various temperatures was determined by evaporating a measured quantity of the solution, and also by titration with potassium permanganate solution in the presence of sulphuric acid. The solubility increased from 0·049 gram per litre at 0° to 0·290 (and 0·252) at 80°. The solution obtained at 80° was discoloured, even after twenty-four hours in a thermostat. This was probably due to partial oxidation of the benzidine, and accounts for the discrepancy between the results obtained by the two methods. The residue obtained at 50° (0·141 and 0·149 gram per litre) was only slightly discoloured, and probably gives the approximate solubility at that temperature. The results show that the smallest possible amount of cold water should be used for washing benzidine sulphate in the quantitative estimation of sulphate. C. A. M.

Simplified Evaluation of Hyposulphite (Blankite; Redo). G. BRUHNS (*Zeitsch. angew. Chem.*, 1920, **33**, 92).—The usual method of estimating hyposulphite by titrating a solution of the salt with potassium ferricyanide is subject to error on account of the rapidity with which the salt is oxidised in solution by atmospheric oxygen. The analysis can be carried out quickly and accurately in the following manner. In a porcelain dish are placed 20 c.c. of a standard potassium ferricyanide solution with a trace of ferrous sulphate sufficient to form a blue colloidal solution but not

a precipitate. A slight excess of the hyposulphite is weighed out in a scoop, and the salt is carefully dusted into the solution, with careful stirring, until the end-point, indicated by a change in colour from blue to bright reddish-yellow, is reached. The scoop is then weighed again to determine the weight of hyposulphite used. The accuracy of the method depends solely on the skill of the manipulator in dusting the powder into the solution. There is a small constant error due to the oxygen dissolved in the ferricyanide solution, but this is probably under 0·5%. E. H. R.

Boric Acid Modification of the Kjeldahl Method for Crop and Soil Analysis. F. M. Scales and A. P. Harrison (*J. Ind. Eng. Chem.*, 1920, **12**, 350—352).—The use of 4% boric acid solution as proposed by Winkler (A., 1913, ii, 527) for absorbing the ammonia in the distillation part of the Kjeldahl method is trustworthy. Bromophenol-blue is a suitable indicator for the subsequent titration. W. P. S.

Method for Estimating Nitrogen in Sodium Nitrate by the Modified Devarda Method and the Use of the Davisson Scrubber Bulb. C. A. Butt (*J. Ind. Eng. Chem.*, 1920, **12**, 352, 354).—The reduction process described by E. R. Allen (A., 1915, ii, 575) is recommended, the scrubber bulb designed by Davisson (A., 1919, ii, 296) being used to prevent alkali spray passing into the receiver. W. P. S.

Estimation of Nitrogen in Calcium Nitrate. E. Platou (*Chim. et Ind.*, 1920, **3**, 310—312).—As manufactured in the Pyrenees by neutralising synthetic nitric acid with limestone, calcium nitrate contains on the average 76·15% of calcium nitrate and 21·45% of water, with small amounts (0·1—0·55%) of other salts of calcium, magnesium, iron, and aluminium. As the material is hygroscopic a fairly large sample (10 to 25 grams) should be dissolved, and portions of the solution taken. The most trustworthy method of estimating the nitrogen is to reduce it in alkaline solution by means of Devarda's alloy, and to distil the ammonia. [See also *J. Soc. Chem. Ind.*, 1920, 401A.] C. A. M.

Estimation of Ammonia in Cultures in Presence of Urea. Pierre Thomas (*Bull. Soc. chim. biol.*, 1919, **1**, 171—175).—To 50 or 100 c.c. of the liquid are added several drops of pure hydrochloric acid and 10% solution of lead acetate until no further precipitation occurs. A little finely powdered lead carbonate is then added, and the whole left for fifteen or eighteen hours. After filtration and washing with cold water, all the ammonia will be found in the filtrate, and the interference of phosphates will be prevented by the preliminary precipitation. The filtrate is introduced into a special form of apparatus, which is illustrated, and 5 grams of magnesium carbonate added. Ammonia is driven off by vacuum distillation below 40°, and is estimated by absorption in standard acid. J. C. D.

Carbonyl Chloride. IV. Estimation of Carbonyl Chloride in Titanium Chloride. M. DELÉPINE and J. LAFORE (*Bull. Soc. chim.*, 1920, [iv], **27**, 290—292).—The method is based on the measurement of the carbon dioxide liberated when the carbonyl chloride is decomposed by water. A special apparatus is described, designed to overcome the difficulty due to the formation of plugs of oxide or oxychloride of titanium at the end of the inlet tube for the sample of titanium chloride. The carbon dioxide is aspirated off, collected in barium hydroxide, and estimated volumetrically. W. G.

Hydrolytic Decomposition of Alkali Aluminates and Methods of Determining the Concentration of Hydroxyl Ions in Concentrated Solutions of Alkali Hydroxides. ROBERT FRICKE (*Zeitsch. Elektrochem.*, 1920, **26**, 129—151).—After a long account of the literature of the hydrolysis of alkali aluminates an account is given of an investigation of the so-called "crystalline" alumina obtained from solutions of the alkali aluminates and of the solutions in equilibrium with the precipitated alumina. Two methods are described whereby, from potential measurements of elements of the type $Hg|Hg_2Cl_2||$ sat. KCl || alkaline solution|PtH, an approximate measure of the hydroxyl ion concentration of highly concentrated solutions of alkali hydroxide may be obtained. By this means it is shown that considerable difference occurs between the hydroxyl-ion concentration of sodium and potassium hydroxides in concentrated solutions. By means of titration experiments it is shown that the hydrolysis of alkali aluminates is a time reaction. The so-called crystalline alumina is not crystalline and possesses properties which vary with the age of the preparation. The ageing of alumina is proportional to the hydroxyl-ion concentration of the alkali solution in equilibrium with it. Measurements on the viscosity of solutions of alkali aluminates indicate that the sodium hydroxide molecule (or the sodium ion) is probably more strongly hydrated than the potassium hydroxide molecule (or the potassium ion). Freezing-point measurements and potential measurements show that aged solutions of aluminates contain considerable quantities of colloidal alumina. J. F. S.

Potassium Chlorate as a Standardising Substance for Solutions of Alkali. H. B. VAN VALKENBURGH (*J. Amer. Chem. Soc.*, 1920, **42**, 757—760).—Potassium chlorate may be used as a standard in titrating alkali by the following method. The chlorate is dried at 240° for four to six hours, the solution is boiled in an Erlenmeyer flask, sulphur dioxide passed in for thirty minutes, and the boiling continued for a further ten minutes to remove all excess of sulphur dioxide. Phenolphthalein is then added, and the solution titrated either hot or cold with alkali. The calculation of the strength of the alkali is based on the equation $KClO_3 + 3SO_2 + H_2O = 3H_2SO_4 + KCl$. The results of titrations by this method agree with those obtained by titrating the alkali with standard acid. J. F. S.

Estimation of Potassium as Perchlorate. II. GREGORY P. BAXTER and MATSUSUKE KOBAYASHI (*J. Amer. Chem. Soc.*, 1920, **42**, 735—742. Compare A., 1917, ii, 270).—The method of estimating potassium by the perchlorate method has, as a result of the publication of Gooch and Blake (A., 1918, ii, 20), been further investigated. The authors maintain the efficiency of the method previously published, with the modification that the initial extraction of the sodium perchlorate should be carried out with alcohol containiug perchloric acid, but not potassium perchlorate, instead of with a saturated solution of the latter salt. When the quantity of sodium is small, the use of a saturated solution of potassium perchlorate for the initial washing is safe, but when the quantity of sodium is large, the potassium salt is best washed once or twice with alcohol containing perchloric acid before the use of the saturated solution of the precipitate is commenced. The chief points to be observed in the estimation are: (i) the use of absolute alcohol; (ii) a low temperature (0° if possible); (iii) filtration in a platinum-sponge crucible; (iv) at least one solution of the precipitate in water and re-evaporation to dryness in the course of the washing; (v) the use of alcohol containing perchloric acid and saturated with potassium perchlorate at the temperature of washing, for washing the precipitate after the sodium salt has been removed by washing with alcohol containing perchloric acid. Using this method, the error is never more than a few tenths of a milligram. J. F. S.

Iodic Acid a Microchemical Reagent for Soluble and Insoluble Compounds of Calcium, Strontium, or Barium. G. DENIGÈS (*Compt. rend.*, 1920, **170**, 996—998).—Iodic acid, in 10% aqueous solution, gives almost immediately finely crystalline, characteristic precipitates of calcium, strontium, or barium iodate with salts of these metals. This serves as a basis for the microchemical detection of these metals. An insoluble salt is finely powdered and suspended in a drop of water on a microscope slide, and a drop of the iodic acid solution is added, the formation of the crystalline precipitate being observed under the microscope. A soluble salt is dissolved in water, one drop of the solution being used. If barium is present as the sulphate, this salt is best reduced by heating it on a platinum wire in a reducing flame, the test being applied to the resulting sulphide. Calcium iodate or periodate should be first ignited to the iodide before applying the test. W. G.

The Spectrographic Detection of Metals and Specially of Zinc in the Animal Organism. A. DE GRAMONT (*Compt. rend.*, 1920, **170**, 1037—1039).—Using the method of spectral analysis previously employed for the detection of titanium (compare A., 1918, ii, 49), zinc may readily be detected in the ash from cobra venom by its rays $\lambda = 4811$ and 4722 and the ultra-violet ray $\lambda = 3345$. The method is also suitable for the detection of traces of iron. W. G.

Rapid Estimation of Copper in Copper-Aluminium Alloys. PIERRE HULOT (*Ann. Chim. anal.*, 1920, [ii], **2**, 103).—A portion of the finely divided alloy is treated with 20% potassium hydroxide solution, which dissolves the aluminium. The insoluble residue of copper is then collected, washed, and weighed, or dissolved in nitric acid, converted into sulphate, and estimated electrolytically. W. P. S.

Detection of Manganese and Zinc in the Presence of Phosphates or Oxalates. E. SCHMIDT (*Ber. deut. Pharm. Ges.*, 1920, **30**, 217—218). Manganese and zinc are precipitated together by means of ammonium sulphide, and are then separated by a method based on the different solubilities of their respective hydroxides, $Mn(OH)_2$ and $Zn(OH)_2$, in a solution of ammonia and ammonium chloride. Wester's statement (this vol., ii, 334) that in the presence of phosphoric or oxalic acid the metals are precipitated as phosphates or oxalates is incorrect, since the precipitates consist of sulphides even under these conditions. This is shown by the fact that on treating a solution of manganese sulphate containing ammonium chloride with ammoniacal ammonium sodium phosphate solution in excess, and then saturating the liquid with hydrogen sulphide, the precipitated manganese phosphate is converted into manganese sulphide. An addition of ammonium sulphide does not effect this conversion under these conditions. C. A. M.

Estimation of Iron in Iron Ores by means of Permanganate. R. SCHWARZ (*Chem. Zeit.*, 1920, **44**, 310—311).—In reply to the criticisms of Brandt (this vol., ii, 269) on the method of Schwarz and Rolfes (A., 1919, ii, 170), experiments are described which show that colloidal silicic acid solutions have no disturbing influence on the results of the titration of iron in sulphuric acid solution. On the contrary, the sol in association with the manganous salt has a favourable influence on the titration of iron in hydrochloric acid solution. There is no evidence of the alleged formation of an intermediate persilicic acd. C. A. M.

Method for the Analysis of an Iron Ore. ERNEST LITTLE and WILLARD L. HULT (*J. Ind. Eng. Chem.*, 1920, **12**, 269—273).—The ore is dissolved in hydrochloric acid, the ferric salts are reduced, and the solution is diluted and treated with an excess of standardised potassium dichromate solution. Five grams of ammonium fluoride and 5 grams of potassium iodide are then added, and the iodine liberated by the excess of dichromate is titrated with thiosulphate solution. The ammonium fluoride prevents the action of the ferric salts on the iodide. The preliminary reduction of the ferric salts may be made with stannous chloride solution (avoiding an excess), mercuric chloride being added afterwards, but the use of the Jones' reductor is recommended. W. P. S.

Use of Cupferron in Quantitative Analysis. G. E. F. Lundell and H. B. Knowles (*J. Ind. Eng. Chem.*, 1920, **12**, 344—350).—Cupferron (the ammonium salt of nitrosophenylhydroxylamine) has been used for the separation of iron from manganese, and iron and titanium from aluminium and manganese, its use has also been found trustworthy for the estimation of iron, copper, titanium, zirconium, thorium, and vanadium. In most cases, however, the "cupferron" method does not offer any advantages over ordinary established methods. The following substances interfere with the separations: silver, mercury, tin, lead, bismuth, cerium, tungsten, uranium, silica, and excessive amounts of phosphorus, alkalis, and alkaline earths. W. P. S.

Influence of Atmospheric Oxygen on the Iodometric Estimation of Chromium. Otto Meindl (*Zeitsch. anal. Chem.*, 1919, **58**, 529—548).—The iodometric estimation of chromium is affected by atmospheric oxygen, since the latter enters into the reaction between the chromic acid and hydriodic acid. The results obtained are too high, the error increasing with the time of contact. W. P. S.

A Test for Molybdenite. F. C. Fuchs (*Informaciones y mem. soc. ing. Peru*, 1918, **20**, 423).—The mineral to be tested is dissolved in fused potassium hydroxide. If molybdenum sulphide is present, it dissolves with an intense red colour. If the fused mass is cooled and dissolved in water, the colour changes to blue, green, yellow, etc., correspouding with the various states of combination of molybdeuum. The reaction is explicable on the theory that molybdenum sulphide gives up one of its sulphur atoms to the fused potassium hydroxide, forming a red, double sulphide.

Chemical Abstracts.

Estimation of Tungsten. R. F. Heath (*Chem. Trade J.*, 1920, **66**, 629).—The sample is fused with sodium peroxide, and the filtered extract of the mass treated with 6—7 c.c. of a solution prepared by dissolving 10·3 grams of stannous and 2·1 grams of stannic chlorides in 100 c.c. of dilute acetic and 40 c.c. of syrupy phosphoric acids. Three to four c.c. of sulphuric acid are added, and, after allowing the blue colour to develop for several minutes, it is compared with that produced by the reagent in solutions of known tungsten content. [See also *J. Soc. Chem. Ind.*, 1920, June.] A. R. P.

Analysis of Tungsten. Joseph Erlich (*Ann. Chim. anal.*, 1920, [ii], **2**, 102—103).—The tungsten is heated with hydrochloric acid and ferric chloride, and the insoluble portion is collected, washed with ammonium nitrate solution, ignited, and weighed. The ignited residue is then fused with sodium hydrogen sulphate, dissolved in ammonia, and the solution treated with ammonium carbonate; the tungstic oxide remains in solution, and

the impurities, which are precipitated, are collected, ignited, weighed, and their weight deducted from the weight first obtained. The difference between the two weights gives the quantity of tungstic oxide present. Two fusions with sodium hydrogen sulphate may be necessary in order to separate all the impurities.

W. P. S.

Estimation of Tungstic Acid in Tungsten Concentrates. HÉRCULES CORTI (*Anal. Soc. Quim. Argentina*, 1917, **5**, 308—326). —A detailed description is given of the estimation of tungstic acid in wolfram or scheelite concentrates by decomposing the finely powdered ore with hydrochloric acid, evaporating to dryness to render silica insoluble, dissolving the tungstic acid in the washed residue with ammonia, evaporating the filtrate, and igniting the residual WO_3. [See *J. Soc. Chem. Ind.*, 1920, June.]

W. R. S.

The Salts of Nitrosophenylhydroxylamine (Cupferron); Uranous Salt. V. AUGER (*Compt. rend.*, 1920, **170**, 995—996).— In neutral solution, cupferron gives precipitates with all the metallic salts except those of the alkali metals, the precipitates obtained being divisible into simple salts, insoluble in chloroform and decomposed by dilute acids, and complex salts, soluble in chloroform and more or less resistant to concentrated acids.

Uranyl salts do not give precipitates with cupferron, but if they are first reduced by zinc to uranous salt, then the whole of the uranium is precipitated in acid solution by cupferron. The *uranous* salt obtained is soluble in chloroform, from which it crystallises in brown prisms, $(C_6H_5O_2N_2)_4U$. Thus, by this means, vanadium and uranium may be separated by successive precipitation. W. G.

The Estimation of Uranium. R. SCHWARZ (*Helv. Chim. Acta*, 1920, **3**, 330—346).—Of the various precipitants recommended for uranium, mercuric oxide is untrustworthy, hydrogen peroxide is quite unsatisfactory, ethylenediamine has no advantages over ammonia, and hydrofluoric and oxalic acids are inconvenient. The simplest and most trustworthy agents are ammonium sulphide and ammonia. Precipitation with the former is best carried out at 80° in presence of ammonium chloride; some ammonium uranate is always formed, and, further, complete separation from the alkali metals is only attained by repeating the precipitation. Precipitation with ammonia should be performed at 100° in presence of ammonium chloride, and preferably not in glass vessels, owing to the tendency of ammonium uranate to carry silica with it. Ignition of the precipitate from either process to uranosouranic oxide (Zimmermann, A., 1886, 598) is best carried out in porcelain crucibles with access of air, since platinum permits diffusion of gases from the flame, and consequent reduction. Its reduction by means of hydrogen to uranous oxide is not quanti-

tative (Kern, A., 1902, ii, 51), owing to the formation of nitride. The separation of uranium from the alkali metals in the form of uranyl phosphate (Kern) was found to be almost impossible owing to the fineness of the precipitate obtained. Of volumetric processes, that involving the solution of uranosouranic oxide in sulphuric acid (Boller, *Diss.*, Zurich, 1915) was simplified and gave good results; this was not the case, however, if complete reduction to urano-salts were first attempted (compare Pulmann, A., 1903, ii, 761). The estimation of uranium in presence of aluminium is most conveniently performed titrimetrically. The precipitation of aluminium by means of ammonium carbonate in presence of ammonium salts is incomplete, and some uranium is also carried down; a complicated procedure, which, however, gives good results, is necessary to effect complete separation. Contrary to Kern's view, Pisani's process (1861) for the separation of iron from uranium by ammonium carbonate and ammonium sulphide is quite effective. Ditte's process (this Journ., 1877, ii, 926) for the separation from chromium salts is unsatisfactory (compare Formánek, A., 1890, 852), and they must first be oxidised to chromate, most suitably by alkaline hypobromite, although Jannasch's ammonium persulphate method gives exact results. Sodium uranate, when precipitated in presence of chromate (Gibbs, this Journ., 1874, 93), always contains uranyl alkali chromates, and the precipitation must therefore be repeated; it is also advisable to redissolve the uranosouranic oxide finally obtained in nitric acid to separate it from silica.

A redetermination of the dissociation tension of uranosouranic oxide gave results differing from those of Colani (A., 1907, ii, 878), and, taken in conjunction with the heat of formation of uranosouranic oxide from uranous oxide (Mixter, A., 1912, ii, 899), indicate the existence of an intermediate oxide. Further, by igniting the higher oxide in a stream of carbon dioxide in an electric furnace at 1122°, a black residue was obtained corresponding approximately in composition with the formula U_2O_5; traces of nitride were produced when nitrogen was employed. The contrary results of Zimmermann (*loc. cit.*) were vitiated by his use of a platinum crucible over a gas flame, which permitted reduction. For the same reason, the ignition of chromic oxide is best carried out in a platinum crucible, since this avoids the formation of chromichromate otherwise observed (Rothang, A., 1914, ii, 73). J. K.

Estimation of Nitroform by Potassium Permanganate. PHYLLIS VIOLET MCKIE (T., 1920, **117**, 646—648).

Reactions of Chloropicrin. GUILLEMARD and LABAT (*Bull. Soc. pharm., Bordeaux*, 1919; from *Ann. Chim. anal.*, 1920, [ii], **2**, 120—121).—The odour of chloropicrin is destroyed by alkali polysulphide solution. When a drop of chloropicrin is boiled with alcoholic potassium hydroxide solution and a small quantity of thymol, a yellow coloration is obtained; if the thymol is replaced by resorcinol, the coloration is red. The addition of sulphuric acid

to the alkaline thymol mixture produces a reddish-violet coloration, and the whole mixture, on dilution with acetic acid, exhibits an absorption band in the green portion of the spectrum. Chloroform yields slightly different colorations under the above conditions, but a mixture of chloroform and a trace of sodium nitrite yields the same reactions as does chloropicrin. Both chloroform and chloropicrin yield a carbylamine. When chloropicrin is boiled with potassium hydroxide solution, the mixture, after cooling, yields reactions characteristic of nitrous acid. W. P. S.

Estimation of Methyl Alcohol. S. B. Schryver and Cyril Christian Wood (*Analyst*, 1920, **45**, 164—170).—A method for the estimation of methyl alcohol in aqueous solution is described, the essential principle of the method being the determination of the concentration of ammonium persulphate necessary to destroy completely the formaldehyde formed in the initial stages of the oxidation process under certain specified conditions of experiment. The formaldehyde is detected by the phenylhydrazine hydrochloride and potassium ferricyanide test described previously by one of the authors (Schryver, A., 1910, ii, 335). By slight modification, the method may be used for the estimation of methyl alcohol in acetone. To estimate methyl alcohol in ethyl alcohol, the mixture of alcohols is oxidised partly by a relatively small amount of persulphate (the alcohols being in excess), and the formaldehyde formed is estimated colorimetrically. [See, further, *J. Soc. Chem. Ind.*, 1920, June.] W. P. S.

Use of Diastatic Reagents in Analytical Investigations. Differentiation between Guaiacol and Creosote. Luciano P. J. Palet (*Anal. Soc. Quim. Argentina*, 1917, **5**, 305—307).—Creosote is known to have been used as a substitute for guaiacol in medicinal preparations. They may be differentiated by dissolving the residue from the chloroform extract of the sample in alcohol and adding a direct oxydase. In presence of guaiacol, a yellow coloration is obtained at once, which gradually turns orange. Creosote under the same conditions gives no colour; after more than half an hour, a slight violet tint develops. If a few drops of hydrogen peroxide are also added to the test, guaiacol gives a more intense colour, whilst creosote furnishes a strong, reddish-violet coloration; indirect oxydases may be used when hydrogen peroxide is added. It is recommended to carry out the reactions in dilute solution. W. R. S.

The Systematic Detection of Acetates. L. J. Curtman, D. A. Broggi, and V. Fourman (*Chem. News*, 1920, **120**, 230).—To detect acetates in mixtures, the following procedure is recommended. The solution is acidified with 10% nitric acid and 5 c.c. in excess added, followed by $N/4$-silver nitrate until no further precipitate is formed. After filtering, the clear liquid is made just alkaline with sodium hydroxide, and 10 c.c. each of $2N$-barium chloride

and $2N$-calcium chloride solutions added. The precipitate is filtered off, and the filtrate evaporated to 5 c.c. after addition of 10 c.c. of 3% hydrogen peroxide. The crystals are filtered off, and the filtrate made just neutral to phenolphthalein with hydrochloric acid. One c.c. of $N/2$-ferric chloride solution is added, and the colour compared against that of 1 c.c. of the reagent in 5 c.c. of water. Two mg. of acetic acid give a pale reddish-yellow colour. The odour of acetic acid is perceptible if 1 c.c. of a solution containing at least 2 mg. of the acid is boiled with 2 c.c. of 1:1 sulphuric acid, but nitrates seriously interfere with the test.

A. R. P.

Estimation of the Total Non-amino-organic Acids in Urine. A. Desgrez and M. Polonowski (*Compt. rend.*, 1920, **170**, 1008—1010).—One hundred c.c. of the urine are made alkaline with sodium carbonate and evaporated to dryness on a water-bath. The residue is mixed with pure sand moistened with a slight excess of phosphoric acid, and the whole is extracted with ether containing 1% of alcohol in a Louïse apparatus for ten hours. To the ethereal extract a known volume of N-sodium hydroxide is added, and the excess is titrated with N-sulphuric acid.

To obtain some idea of the molecular weight of the non-amino-acids and to correct for any hydrochloric acid present, the ethereal extract is shaken several times with a solution of barium hydroxide. The insoluble barium salts are collected, washed, dried at 110°, weighed, ignited to barium carbonate, and weighed again. These two weighings give a means of calculating the average molecular weights of the barium salts insoluble in water. The filtrate from the above precipitate is freed from excess of barium by carbon dioxide, and the solution is filtered, evaporated to dryness, and the residue weighed. By calcination, the organic barium salts are converted into carbonates, and the residue is again weighed. The carbonate is converted into chloride, and the total chloride is dried and weighed. The three weighings allow of a calculation of the amount of chloride mixed with the organic salts, the total weight of the latter, and their average molecular weight.

W. G.

A New Reaction of Acraldehyde. Lucas Tsalapatanis (*Anal. Soc. Quim. Argentina*, 1917, **5**, 244—245).—The liquid to be tested is heated with 1—2 c.c. of an aqueous solution of resorcinol and a few drops of 10% sodium hydroxide solution. After two minutes, a bluish-green coloration appears in dilute, and a red one in concentrated, solutions. The reaction is extremely sensitive. The colour, which is very stable, is destroyed by acids, but restored by sodium hydroxide.

W. R. S.

Microchemical Method for the Estimation of Sugar in Body Fluids. R. Goiffon and F. Nepveux (*Compt. rend. Soc. Biol.*, 1920, **83**, 121; from *J. Pharm. Chim.*, 1920, [vii], **21**, 357—359).—A portion of the fluid, after suitable clarification, is boiled with Fehling's solution, the cuprous oxide is collected,

washed, dissolved in a minimum quantity of hydrochloric acid, a few drops of potassium ferrocyanide solution and three drops of saturated tartaric acid solution are added, and the coloration obtained is compared with those shown by standards prepared under similar conditions from known amounts of sugar.

W. P. S.

The Iodometric Estimation of Sugars. HILDA MARY JUDD (*Biochem. J.*, 1920, **14**, 255—261).—Estimation of lævulose in fruit juices by the polarimetric method is untrustworthy. Various iodometric methods for the estimation of aldoses in the presence of ketoses have been tested, and none of them was found to give quantitative results. This is ascribed to the action of the dilute alkalis on the sugars. In using either the method of Colin and Liévin (A., 1918, ii, 461), or that of Willstätter and Schudel (A., 1918, ii, 337), a definite and constant weight of iodine always reacts with a given weight of dextrose. This weight of iodine is not affected by the changes in the amount of alkali present, or by the presence of other sugars. This is also true of lævulose. It is therefore possible to calculate the amount of dextrose and lævulose in a solution from the copper-reducing power and the iodine figure. Each sugar has its own characteristic iodine value. Rhamnose behaves very abnormally. Sucrose is not oxidised, whilst lactose and maltose are both oxidised, the former requiring twice as much iodine as the latter. J. C. D.

Estimation of Sugars by Inversion. E. HILDT (*Ann. Chim. anal.*, 1920, [ii], **2**, 103—106).—A discussion regarding methods for the inversion of sugars. Chemical catalysts possess advantages over enzymes, since they have a definite action under given conditions. Certain aromatic sulphonic acids (benzenesulphonic acid, etc.) are particularly useful for this purpose, especially in the estimation of sugars in sweetened condensed milk.

W. P. S.

A Cryoscopic Method for the Estimation of Sucrose. HENRY H. DIXON and T. G. MASON (*Sci. Proc. Roy. Dubl. Soc.*, 1920, **16**, 1—8).—The method consists in determining the freezing point of the solution before and after the inversion of the sucrose by invertase. The freezing point is determined by the thermo-electric method described by Dixon (compare A., 1911, ii, 853). In the case of plant sap, the tissues are frozen and the sap pressed out. The sap is boiled and filtered, and weighed quantities are cooled in test-tubes to $-2°$. The requisite amount (0·33 gram) of invertase is added and the freezing point determined. The mixture is then incubated at 28° for twenty-four hours and the freezing point again determined. The increase in the depression of the freezing point is a measure of the sucrose originally present. A preliminary removal of gums, etc., from the sap is not necessary. Using 2·5 c.c. of sap the probable error is 0·0016 gram of sucrose. W. G.

Estimation of Amino-acids by means of the Hydrogen Electrode. E. L. Tague (*J. Amer. Chem. Soc.*, 1920, **42**, 174—184).—Neutralisation curves have been obtained for the amino-acids, lysine dihydrochloride, glutamic acid, tyrosine, phenylalanine and glycine. The method consists in adding standard alkali hydroxide solution to a definite volume of an aqueous solution of the acid and measuring the hydrogen-ion concentration after each addition; this process is continued until the solution has a P_H value of 12·5. Then to an equal volume of water, proceeding in the same way, the same standard alkali is added until the same P_H value is obtained, care being taken to add sufficient water to give the blank the same volume as that of the original solution at the P_H value. Subtracting the number of c.c. used in the blank from that required in the original titration gives the number of c.c. of standard alkali necessary to neutralise the amino-acid alone. In this way it is possible to obtain the neutralisation curves of the amino-acids alone, and the influence of the different groups may be seen. Certain inaccuracies in the formalin titration method are explained by this method. An hydroxyl-ion concentration of about 2×10^{-2} ($P_H = 12·5$) will suppress the basic ionisation of the sodium salts of the amino-acids to a negligible extent, and thus make it possible to obtain a more exact quantitative estimation of the diamino-acids as well as of others containing strongly negative groups. J. F. S.

Method of Graduating Ureometers of the Yvon Type. Ch. O. Guillaumin (*J. Pharm. Chim.*, 1920, [vii], **21**, 342—346).—The ureometer is supported vertically with the tap at the lower end, and is filled with water; the open end is closed by a rubber stopper through which passes the end of a very narrow, graduated tube about 18 cm. long and having a capacity of 2 c.c. The ureometer is then turned so that the tap is at the top, the level of the water having been adjusted previously to the zero mark on the graduated tube, and small quantities of air are admitted successively through the tap, the volumes of these quantities being given by the changes in level of the water in the graduated tube.

W. P. S.

Braunstein's Modification of the Mörner-Sjöqvist Process for the Estimation of Urea. Alan Herepath Todd (*Biochem. J.*, 1920, **14**, 252—254).—This modification (A., 1901, ii, 140) does not give a quantitative yield of urea nitrogen. Ignition of the filtrate for fourteen hours at 185° with 15 grams of crystalline phosphoric acid gives an accurate result. J. C. D.

Estimation of Uric Acid by a Modification of Blarez and Tourrou's Method. G. Pégurier (*Ann. Chim. anal.*, 1920, [ii], **2**, 109—110).—Fifty c.c. of urine are treated with 5 c.c. of saturated sodium carbonate solution, and the mixture is added

slowly to 5 c.c. of Fehling's solution decolorised previously by the careful addition of sodium hydrogen sulphite solution. The precipitate which forms is collected on a filter, and washed with water; the filter and precipitate are then transferred to a beaker containing 150 c.c. of water and 10 c.c. of dilute sulphuric acid (1:1), and the mixture is titrated with 0·212% potassium permanganate solution. Each c.c. of the latter corresponds with 0·1 gram of uric acid per litre of urine. W. P. S.

Action of the Arsenotungstic Reagent on certain Alkaloids and Glucosides. LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1916, **4**, 256—258).—The arsenotungstic reagent for phenolic groups proposed by Guglialmelli (A., 1916, ii, 584) has been applied to a large number of alkaloids and glucosides, and the result is tabulated in the original. W. R. S.

Forensic Investigation of Aconitine. Its Resistance to Putrefaction. LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1918, **6**, 480—487).—A rat was killed by subcutaneous injection of 0·002 gram of aconitine. The carcase was left to putrefy seven days in the air, and subsequently buried during two months in a metal box. The pulped viscera were treated with absolute alcohol, slightly acidified with 10% tartaric acid, and kept for fifteen minutes at 50°; the cooled liquid was filtered and distilled in a vacuum; the residue was left overnight in contact with 250 c.c. of absolute alcohol, the liquid filtered, and distilled in a vacuum. This treatment was repeated twice. The final residue was dissolved with 200 c.c. of water, which was distilled off to remove alcohol, again dissolved in water, and filtered. This liquid was extracted in a separator (1) with ether, (2) with ether after previous addition of sodium hydrogen carbonate to feebly alkaline reaction, and (3) with chloroform. The last extract was evaporated and the residue treated with 10% acetic acid. It gave positive reactions with Mayer's and Monti's reagents, had the characteristic action on the tongue, and gave a violet coloration with a solution of 1 gram of sodium molybdate in 25 grams of phosphoric acid. Brouardel and Boutmy's reaction for ptomaine was negative. The conclusions are: that aconitine is not destroyed by the natural blood ferments; that it resists putrefaction for two months; that weak acids and alkalis should be used for its extraction; that its characterisation may be effected by the organoleptic test and the reaction with phosphoric acid and sodium molybdate; that crystallised aconitine does not give a violet coloration with officinal phosphoric acid, either hot or cold. W. R. S.

Test for Strychnine. H. E. BUC (*J. Assoc. Off. Agric. Chem.*, 1919, **3**, 193).—One gram of zinc amalgam and 0·5 c.c. of hydrochloric acid are added to 0·5 c.c. of the strychnine salt solution; after fifteen minutes, the liquid is decanted and treated, drop by drop, with 0·02% potassium ferricyanide solution. A pink to rose-red coloration is obtained. The zinc amalgam is prepared by

washing granulated zinc with hydrochloric acid, treating it for one hour with 1% potassium antimonyl tartrate solution, and then adding mercuric chloride solution and a small quantity of hydrochloric acid; after thirty minutes, the zinc is removed from the solution, washed, and dried. The test will detect 0·001 mg. of strychnine provided that interfering substances, such as large amounts of other alkaloids and certain organic substances, are absent.

W. P. S.

Use of Ethyl Acetate as a Precipitating Reagent for Proteins. A. Marie (*Ann. Inst. Pasteur*, 1920, **34**, 159—161).—Ethyl acetate gives a marked precipitate with even dilute solutions of proteins, and a turbidity with peptones, proteoses, or albumoses, but solutions of amino-acids or vegetable or animal alkaloids show no apparent change in their physical state on its addition. W. G.

Important Source of Error in Investigating Urines for Albumin by means of Sulphosalicylic Acid. Schall (*Münch. med. Woch.*, 1920, **67**, 164—165; from *Chem. Zentr.*, 1920, ii, 582—583).—It is found that sulphosalicylic acid gives a precipitate with urines rich in calcium which may easily be mistaken for a positive albumin reaction. The distinction between precipitated calcium sulphate and albumin is most readily made if the urine is previously diluted with at least half its volume of water; under these conditions calcium sulphate is not precipitated, whilst the albumin reaction is but little affected. H. W.

Estimation of the Fibrin, Globulin, and Albumin Nitrogen of Blood Plasma. Glenn E. Cullen and Donald D. Van Slyke (*J. Biol. Chem.*, 1920, **41**, 587—597).—Fibrin is estimated by precipitation with calcium chloride under definite conditions from plasma containing 0·5% potassium oxalate. After thorough washing, the precipitate is submitted to the Kjeldahl process.

Albumin is estimated in plasma by precipitating the globulin by half saturation with ammonium sulphate, quantitatively removing the excess of ammonia in the filtrate, and making a Kjeldahl estimation on the residue. Non-protein nitrogen is estimated after removal of the plasma proteins by trichloroacetic acid. The plasma proteins are, therefore, separately estimated as follows: Fibrin N, directly; globulin N = total N − (filtrate N + fibrin N); albumin N = filtrate N − non-protein N. J. C. D.

Crystallisation of Hæmatoporphyrin. Th. Lochte and E. Danziger (*Vierteljahrschrift ger. öffentl. Sanitätswesen*, **59**, 140—143; from *Chem. Zentr.*, 1920, ii, 396—397).—The method described depends on Willstätter's process, and is effected in the following manner. The spot of blood is removed as completely as possible and covered in a small test-tube with about 0·5 c.c. of hydrobromic–glacial acetic acid solution; the tube is corked and heated at 40—50° for about fifteen minutes. After remaining for thirty-six to forty-eight hours at the ordinary temperature, water

is added, followed by sodium hydroxide solution sufficient to neutralise the acid; the solution is faintly acidified with acetic acid and extracted two to three times with ether. The ether is allowed to evaporate slowly on a small watch-glass, the residue is washed into the centre of the glass with two or three drops of alcohol, and then treated with three to five drops of concentrated *hydrochloric acid*. The watch-glass is covered with a larger dish, and the solution is allowed to evaporate slowly; crystals generally form within one or two days. H. W.

Colorimetric Estimation of Stercobilin. R. Goiffon (*Compt. rend. Soc. Biol.*, 1920, **83**, 60; from *J. Pharm. Chim.*, 1920, [vii], **21**, 286—288).—Stercobilin, a reduction product of *bilirubin, yields a red-coloured mercury compound which is soluble* in dilute ammonia. To estimate stercobilin in fæces, 40 c.c. of a 10% fæcal solution are heated for one hour at 50° with 5 c.c. of saturated mercuric chloride solution; the warm mixture is then treated with 2 c.c. of ammonia, diluted to 50 c.c., filtered, and the coloration of the filtrate compared with that of a standard. The latter may consist of a mixture of 100 c.c. of 10% cobalt chloride solution and 5 c.c. of potassium dichromate solution. The value 10 is suggested as a normal when the colorations of the test and standard solutions are of equal intensity. W. P. S.

Colloid-chemical Considerations regarding the Reductase Test for Milk. Egon Eichwald (*Zeitsch. Nahr. Genussm.*, 1919, **38**, 359—361).—It is pointed out that the colloids in milk may *play a part in the methylene-blue test for reductase in milk, and* preliminary experiments show that the finer the state of division of the colloids (proteins and fat), the slower is the rate at which the blue colour is destroyed. W. P. S.

Reduced Eosin and Potassium Persulphate. León Goldenberg (*Anal. Soc. Quim. Argentina*, 1917, **5**, 264—266).—A colourless solution of reduced eosin may be obtained almost instantly and in the cold by weighing 1 gram of eosin, dissolving 2 grams of sodium hydroxide in 100 c.c. of water redistilled in glass, adding part of the eosin and 5 grams of chemically pure zinc dust, and shaking until decolorisation is complete. The remainder of the eosin is then added in portions whilst shaking. The stock solution thus obtained may be kept for two to three weeks, after which the eosin acquires a yellow colour on regeneration. For investigating oxydases, 0·5 c.c. of the above solution is made up to 100 c.c. The incomplete decolorisation of eosin by commercial zinc dust and distilled water condensed in metallic receivers is due to the presence of copper, traces of which are sufficient to induce catalytic re-oxidation of the reduced eosin.

The oxidising action of oxydases may be measured by comparison with a *N/100-solution of potassium persulphate*, 1 c.c. of which furnishes 0·00016 gram of oxygen. The quantity of oxydase which

causes reduced eosin to absorb 0·00016 gram of oxygen in one hou at 37° is called the "oxydasogenous unit." As the solutions i which oxydases are determined are generally too turbid for com parison with the standard regenerated by persulphate, the regene ated eosin obtained in the determination is best precipitated by 2· hydrochloric acid, collected on a double paper, washed with th acid, and redissolved on the filter in 2—3% sodium hydroxide. Th clear filtrate may now be matched against the persulphate standar

W. R. S.

Quantitative Measurement of Lipase and Amylase i Pancreatic Juice. H. MAUBAN (*Compt. rend. Soc. Biol.*, 192 **83**, 130; from *J. Pharm. Chim.*, 1920, [vii], **21**, 355—357).—Tw c.c. of 0·2% starch solution are placed in each of ten tubes, and t the first is added 1 drop of pancreatic juice, to the second tube drops, and so on. The tubes and their contents are heated at 37 for five minutes, 0·25 c.c. of Fehling's solution is then added t each, and the mixtures are boiled for one minute, a small quantit of potassium ferrocyanide being added to prevent precipitation c copper. In this way is found the quantity of pancreatic juic necessary to produce sugar just sufficient to decolorise the measure quantity of Fehling's solution. Six or seven drops of norm pancreatic juice are usually required. W. P. S.

Estimation of Soil Acidity and Alkalinity by means c Indicators in the Field. EDGAR T. WHERRY (*J. Washingto Acad. Sci.*, 1920, **10**, 217—223).—The method of estimating th acidity or alkalinity of a soil in terms of P_H (A., 1919, i, 428) ha been adapted for use in field tests, and a table has been construct showing the reactions of the soil corresponding with the colou changes of a series of indicators, each of which overlaps the ne in the scale. Passing from extreme acidity to extreme alkalinit these indicators and their corresponding P_H values are: *Brom phenol-blue*, dull green, 3·5; brownish-green, 4·0; violet, 4·5 *methyl-red*, violet, 4·5; red, 5·0; orange, 5·5; yellow, 6·0; *brom cresol-purple*, yellow, 5·5; brownish-green, 6·0; violet, 6·5; purpl 7·0; *bromothymol-blue*, yellow, 6·0; greenish-yellow, 6·5; green, 7·0 blue, 7·5; *phenol-red*, yellow, 6·5; orange-yellow, 7·0; orange, 7·5 red, 8·0; violet-red, 8·5; *phenolphthalein*, colourless, 8·0; pale pin 8·5; deep pink, 9·0; violet-red, 9·5. A definite quantity of the so is shaken with neutral salt-free water, and the clear extract teste with successive indicators until one indicator shows an intermedia colour or the extreme colorations of two successive indicators ove lap, and the corresponding P_H value is obtained from the table. B treating standard solutions of known ionic concentration and com paring the colorations with those given by soil extracts with th same indicators, specific acidities differing by a factor of $\sqrt[5]{10}$ 1·59 ($P_H = 0·2$) may be distinguished, but in practice values diffe ing by a factor of $\sqrt{10}$ or 3·16 ($P_H = 0·5$) are sufficiently accurat since the reactions of the soil from different parts of the root of th same plant may differ by a factor of 10 or more. C. A. M.

General and Physical Chemistry.

Relation between the Refractivity and Density of Carbon Dioxide. P. PHILLIPS (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 225—240).—The density and refractive index of carbon dioxide have been determined at 34°, under such conditions as allowed a gradual change in density from 0·73 gram/cm.^{3} downwards, with the object of testing the validity of the Lorenz and Lorentz formula. The experiments were made by means of a small Fabry and Perot etalon, and the density values were deduced from the total amount of gas used and the volume of the containing vessel. From measurements with the mercury lines λλ 5790, 5461, and 4358×10^{-8}, it is shown that the reciprocal of the Lorenz and Lorentz constant is a linear function of the square of the density. For the wave length 5461×10^{-8}, the relation between the refractive index and the density is $(\mu^2+2)\rho(\mu^2-1)=6{\cdot}581+0{\cdot}1130\rho^2$.

J. F. S.

Maxwell's Relation between the Refractive Index and Dielectric Constant and a Method of Determining Ionic Charges in Crystals. M. BORN (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1918, 604—613).—On the space-lattice theory of the author, it is shown that the product of the ionic charge and the wave-length of the lattice-vibration in diatomic crystals may be expressed by the difference $D-n_r^2$, where D is the dielectric constant and n_r the nearly constant value of the refractive index between the short- and long-wave infra-red specific frequencies ("Eigenschwingungen"). By comparison with the wave-lengths of the residual-rays ("Reststrahlen"), an approximation to the ionic charge is obtained which is in moderate agreement with that of the electrolytic ions.

J. R. P.

Reflection Capacities and Dielectric Constants of Insulating Solids and Liquids. H. RUBENS (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1915, 4—20).—The simple relation between reflecting capacity in the infra-red and the electric conductivity of metals deduced by Maxwell had been confirmed in previous experiments. The analogous relation between reflecting capacity and dielectric constant was confirmed in the case of twenty-five solid insulators with eight different wave-lengths in the infra-red. The insulating liquids examined exhibited an entirely different relation, which is explained by a theory due to Debye, that part of the abnormally high dielectric constant arises from the orientation of the electric dipoles assumed to exist in the molecules.

J. R. P.

Reflection Capacity and Dielectric Constants of some Amorphous Substances. H. Rubens (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1916, 1280—1293).—Measurements made on fifteen amorphous substances, mainly glasses, led to the result that, for infra-red radiation of long wave-length, the reflection capacities are in close agreement with those calculated from Fresnel's theory from the dielectric constants for slowly varying fields. Anomalous dispersion in the region of Hertzian waves could not in any case be detected. J. R. P.

Optical Properties of some Crystals in the Long-wave Infra-red Spectrum. I. and II. Th. Liebisch and H. Rubens (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 198—219, 876—900).—I. The reflection capacity of doubly-refracting crystals between the wave-lengths 22μ and 300μ, and the connexion between the electric and optical properties were determined. The results enable the frequency and strength of the corresponding vibrations in the space-lattice to be calculated.

II. Forty-eight crystals of different systems, excluding triclinic, were examined in the manner described in the previous abstract. The positions of the optic axes in adularia and gypsum were determined for ten different wave-lengths, and the gradual change of these axes in the direction of the axes of greatest and least dielectricity was found to be in agreement with the electromagnetic theory. J. R. P.

Critical Study of Spectral Series. V. Spectra of the Monatomic Gases. W. M. Hicks (*Phil. Trans.*, 1920, [*A*], **220**, 335—468. Compare A., 1910, ii, 86; 1912, ii, 512; 1913, ii, 810; 1915, ii, 499).—A theoretical paper in which the series relationships in the spectra of neon, argon, krypton, xenon, and radium emanation are examined mathematically. A table of spectrum constants, in which the most important numerical factors are contained, is given in the paper. The value of the oun in the various cases is neon, 14·47013; argon, 57·9209; krypton, 249·536; xenon, 611·0100; and radium emanation, 1787·024. J. F. S.

Excitation of the Band Spectrum of Nitrogen by Electrons of Feeble Velocity. Léon Bloch and Eugène Bloch (*Compt. rend.*, 1920, **170**, 1380—1382).—From a spectrographic study under special conditions, it is shown that it is possible to excite the radiation of nitrogen with a critical potential of about 10 volts, the band spectrum thus being excited by electronic shock under a voltage decidedly lower than the potential of ionisation (18 volts). W. G.

Measurements of Wave-lengths in the Spectra of Krypton and Xenon. Paul W. Merrill (*Bur. Standards, Bull.*, 1919, **15**, 251—257; *Sci. Paper* No. 345).—This paper records photographic measurements of wave-lengths in the spectra of krypton and xenon,

principally in the red and infra-red. In krypton thirty-seven new lines were measured between 6576 Å and 8928 Å; in xenon fifty-two new lines between 6318 Å and 9162 Å. In this region there are numerous strong lines which are probably among the most important in the spectra of these elements. The xenon lines at 8231 Å and 8280 Å are especially notable. These and other lines may be of value as wave-length standards in the infra-red. Attention is called to a probable analogy between the spectra of the rare gases neon, argon, krypton, and xenon that this investigation has brought to light, which is shown in the tendency of the lines to form groups the position of which apparently has some relation to the atomic weight. CHEMICAL ABSTRACTS.

Absorption Spectra of Metal Ammine Complexes. III. Absorption Spectra of Complex Salts of Nickel, Chromium, and Copper. YUJI SHIBATA and K. MATSUNO (*J. Coll. Sci. Tokyo*, 1920, **41**, 6, 1—37. Compare A., 1919, ii, 381; this vol., ii, 141).—The absorption spectra of a large number of chromium complex ammines, complex sulphates and oxalates, simple chromic salts and complex perchromic derivatives have been measured. Similar measurements have been made for nickel ammines, simple nickel salts, complex pyridine copper derivatives, copper ammines, and simple copper salts. The complex chromic compounds are shown to be stable in aqueous solutions and to give generally two or three sharp absorption bands. They are in every way comparable with the complex cobalt derivative as regards the absorption spectrum. The complex nickel compounds are generally unstable in aqueous solutions; the absorption spectra were, therefore, determined in ammoniacal solution. They exhibit, in every case, two absorption bands, but the absorption is much less strong than in the case of the metals previously examined. The absorption of the complex nickel compounds follows the same laws as that of the complexes of chromium and cobalt. The complexes of copper are the most labile in aqueous solution, and the anion exerts some influence on the absorption in this case. They give no hands, but there is general absorption in both the red and violet ends of the spectrum.
J. F. S.

Ultra-violet Spectrophotometry of the Nitrophenols. FRED VLÈS (*Compt. rend.*, 1920, **170**, 1242—1245).—The spectrum of the nitrophenols in the region studied, $\lambda = 250\ m\mu$ to the visible spectrum, is constituted in general by three elements, namely, (1) an absolutely constant *N*-band due to the absorption of the nitro-groups; this band appears to be formed by two components; (2) a band ϕ, sometimes uncertain, due to the phenolic radicle; (3) a band ψ, inferior to the region studied, and the origin of which is problematical. The constitution in wave-lengths of the spectrum of a compound will be given by the characteristics of the isolated components, slightly modified by coefficients which will depend on the stereochemical properties of the compound. W. G.

Absorption in Respect to the Properties of the Nitrophenols. FRED VLÈS (*Compt. rend.*, 1920, **170**, 1316—1318).—A continuation of previous work (preceding abstract) in which it is shown that it is possible to calculate the absorption spectrum curves of the nitrophenols simply from their constitution and the properties of their constituent groups. W. G.

Abnormal Rotatory Dispersion. G. BRUHAT (*Ann. Physique*, 1920, [ix], **13**, 25—48).—The first part of the paper is a mathematical discussion of the general conditions which a spectropolarimeter should satisfy. The second part is a study of certain coloured tartrates, uranyl tartrate, didymium tartrate in ammoniacal solution, and the cobalt tartrates. The results obtained confirm Natanson's law and the law previously enunciated by the author (compare A., 1915, ii, 302, 503). W. G.

Photochemical Activity of Absorbed Radiations. CHR. WINTHER (*Danske Vid. Selsk. Math. Phys. Medd.*, 1920, **2**, No. 3, 1—35; from *Chem. Zentr.*, 1920, i, 722).—The law of critical activity explains the peculiar fact observed by Warburg (this vol., ii, 210) that the "specific photochemical effect" is of the same order of magnitude for a series of very dissimilar processes. By its aid, the sensitiveness towards light of a particular reaction can frequently be approximately estimated when only its temperature-coefficient in darkness is known. It also affords a ready explanation of the generally observed small temperature-coefficients of photochemical processes and of their increase with increasing wave-length, and also indicates the possibility of chemi-luminescence. It possibly also explains the empirical observation that a process is more susceptible to optical sensitivation for a given wave-length when it is least sensitive to this wave-length. H. W.

Energy-changes during Photochemical Reactions in Gases. IV. Influence of the Wave-length and Pressure on Photochemical Ozonisation. E. WARBURG (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1914, 872—885. Compare A., 1911, ii, 834; 1912, ii, 315; 1913, ii, 652).—The amount of ozone produced in oxygen by ultraviolet light of wave-length $0·253\,\mu$ is smaller, per calorie absorbed, than with light of wave-length $0·209\,\mu$. It is smaller under a pressure of 300 kg. per sq. cm. than under a pressure of 125 kg. per sq. cm. Both results are in contradiction to Einstein's law of photochemical equivalence, which requires considerable modification to accord with experiment. Of the original assumptions of Einstein, (1) that only one quantum is absorbed, (2) that all absorbing molecules are decomposed, the first may for the present be retained, but the second may be modified by assuming that only a portion of the absorbing molecules are decomposed. J. R. P.

Energy-changes during Photochemical Reactions in Gases. V. Absorption of Ultra-violet Radiation by Oxygen. E. WARBURG (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1915, 230—242).—Between pressures of 30 to 400 atm., large deviations

rom Beer's law were found. The molecular absorption of oxygen icreases appreciably with the pressure. The increase is greater or the shorter (0·209 μ) than for the longer (0·253 μ) of the waves sed, and was greater in pure oxygen than in mixtures of oxygen nd nitrogen. The deviations are explained by a theory of K. ngström (*Arkiv. Math. Astron. Fysik*, 1908), according to which ley are due to molecular collisions, and are represented by ormulæ. J. R. P.

Energy-changes during Photochemical Reactions in Gases. I. Photolysis of Hydrogen Bromide. E. WARBURG (*Sitzngsber. Preuss. Akad. Wiss. Berlin*, 1916, 314—329).—The iotolysis of hydrogen bromide by the wave-lengths 0·209 μ and 253 μ follows Einstein's law of photochemical equivalence; the iotochemical action per unit of energy absorbed increases with ie wave-length, and nearly in the ratio required by the theory. ie law can hold only when the work required in the decomposition the molecule is smaller than the quantum of the decomposing diation. This relation is fulfilled with hydrogen bromide with e two wave-lengths used, but is not fulfilled in the photolysis of amonia by the wave-length 0·209 μ and of oxygen by the wavegth 0·253 μ. The deviations found in the last two cases are erefore explained. J. R. P.

Energy-changes during Photochemical Reactions in Gases. II. Photolysis of Hydrogen Iodide. E. WARBURG (*Sitzgsber. Preuss. Akad. Wiss. Berlin*, 1918, 300—317).—The fulfilnt of Einstein's law of photochemical equivalence was demonated with hydrogen iodide with the wave-lengths 0·207 μ, 0·253 μ, d 0·282 μ. J. R. P.

Energy-changes during Photochemical Reactions. VIII. iotolysis of Aqueous Solutions and the Law of Photoemical Equivalence. E. WARBURG (*Sitzungsber. Preuss. Akad. iss. Berlin*, 1918, 1228—1246).—Aqueous solutions of nitrates alkalis and alkaline earths are converted by photolysis into rites. The specific photochemical action is considerably greater weakly alkaline than in weakly acid solutions, increases with the icentration of nitrate, and is greater for shorter than for longer ves, in contradiction to Einstein's law of photochemical iivalence. J. R. P.

Energy-changes during Photochemical Reactions. IX. otochemical Transition of Isomerides. E. WARBURG (*tzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 960—974).—The iversion of maleic into fumaric acid under the influence of wavegths 0·207 μ, 0·253 μ, and 0·282 μ in aqueous solutions was died. The results indicated that the extension of the law of otochemical equivalence (see IV, this vol., ii, 404) does not lead quantitative results, but serves as a guide to the theoretical erpretation of the experiments. J. R. P.

Photochemical Dissociation of Ferric Chloride. ERNESTO PUXEDDU (*Gazzetta*, 1920, **50**, i, 154—161).—Exposure to direct sunlight of a dilute solution of ferric chloride in pure anhydrous ether results in almost instantaneous reduction of the salt to ferrous chloride. No reversion of this reaction occurs in the dark, the chlorine liberated during the reduction being completely used up, partly in chlorinating the ether, apparently to a mixture of the dichloro- and trichloro-derivatives, and partly in oxidation processes with formation of aldehydes; the latter undergo polymerisation to some extent.

In moderately concentrated ethereal solution, ferric chloride is slowly reduced to a mixture of ferrous chloride and a brownish-black organic iron compound containing 2·8% of the metal, and only if this compound is gradually removed is complete reduction possible. T. H. P.

The Disruption of Atoms by α-Rays. G. S. FULCHER (*Science*, 1919, **50**, 582—584).—In Rutherford's recent papers on the nuclear bombardment of light atoms by α-particles, he finds that the ranges of the swiftly accelerated nitrogen and oxygen atoms correspond fairly closely with those to be expected if the swift particles consisted of the singly charged nitrogen and oxygen atoms. The author points out that this requires that the other outriding electrons should accompany the parent atom in its swift motion, which is open to twofold objection. First, a velocity approaching 10^9 cm. sec.$^{-1}$ could not be imparted to the electrons in less than 10^{-18} sec. The strength of the field not being great enough to overcome the inertia of the electrons, they would be left behind initially. Secondly, admitting that the first contention is wrong, the author believes that the outriding electrons would soon be brushed off by the large number of atoms encountered in the long range of flight. As an alternative, the possibility is suggested that the nitrogen atom, presumably composed of hydrogen and helium atoms, is entirely disrupted, and that the particles observed by Rutherford are really doubly charged helium atoms or α-particles. The additional energy necessary to give them a range greater than that of the initial bombarding α-particles would come from the internal energy of the atom in the moment of its disruption, and the phenomenon would constitute a type of artificially produced radioactivity. One difficulty of the author's assumption is to account for the large number of particles which take the same direction as the initial α-particles. He believes this difficulty will not prove insurmountable. Examination of the e/m value of the particles will determine whether Rutherford is correct.

CHEMICAL ABSTRACTS.

***X*-Ray Spectra of the Elements.** R. WHIDDINGTON (*Phil. Mag.*, 1920, [vi], **39**, 694—696).—A theoretical paper in which the speed of the electron (v) carrying the same energy as the α-lines of the K and L spectra of the elements is shown to be fairly well represented by the formula $v = C . N + D$, where N is the atomic

number of the element and C and D are constants determined by the series. For the K series $v=2(N-2)10^8$ cm./sec., and for the L series $v=(N-15)10^8$ cm./sec. The values of $v\times10^{-8}$ and $2(N-2)$ and $v\times10^{-8}$ and $(N-15)$ are compared, respectively, in the K series (nine elements) and in the L series (seven elements), when a very fair agreement is obtained. J. F. S.

The Fine Structure of X-Ray Spectra. M. DE BROGLIE (*Compt. rend.*, 1920, **170**, 1245—1246).—As in the case of the X-ray spectrum of tungsten (compare this vol., ii, 344), it is found that the rhodium spectrum contains a ray which really consists of two components, for which $d\lambda=0{\cdot}0006$ Ångström. W. G.

Spectrum of X-Rays from an Aluminium Target. W. DUANE and TAKEO SHIMIZU (*Physical Rev.*, 1919, **14**, 389—393).—The general radiation spectrum of aluminium for wave-lengths from $0{\cdot}1820\times10^{-8}$ to $1{\cdot}259\times10^{-8}$ cm. has been carefully examined for characteristic radiation which might belong to the J-series of short wave-lengths found by Barkla. No characteristic radiation was found that could not be attributed to molybdenum from the tube or lead from the jaws of the slit. CHEMICAL ABSTRACTS.

X-Ray Absorption Frequencies Characteristic of the Chemical Elements. WILLIAM DUANE and KANG-FUH-HU (*Physical Rev.*, 1919, **14**, 516—521).—The critical absorption frequencies in the K-series for the elements from bromine ($N=35$) down to manganese ($N=25$) were measured. Using these and other data, it is shown that for the elements from cerium to magnesium the square root of the critical frequency is not quite a linear function of the atomic number, N. The deviations amount to several units %. However, the critical velocities, calculated from the quantum relation $\frac{1}{2}mv^2=h\nu$, using the transverse relativity mass $m=m_0[1/\sqrt{1-(v/c)}]$, are found to be linear with N to within about one-fifth %. CHEMICAL ABSTRACTS.

X-Ray Absorption Frequencies Characteristic of the Chemical Elements. W. DUANE and TAKEO SHIMIZU (*Physical Rev.*, 1919, **14**, 522—524).—The measurements of critical K absorption frequencies for the elements from lead ($N=82$) to neon ($N=60$) were made. The deviation from linearity of the sq. root of the frequency with N is much greater than for the lighter elements. This is also true of the deviations of the critical velocity as measured by Duane and Kang-Fuh-Hu (preceding abstract). CHEMICAL ABSTRACTS.

Relation between the Intensity of General X-Radiation and the Atomic Number of the Anticathode. W. DUANE and TAKEO SHIMIZU (*Physical Rev.*, 1919, **14**, 525—529).—The intensity of the general X-radiation from the four elements iron, cobalt, nickel, and copper was measured and found to be proportional to the atomic number rather than to the atomic weight.

These four elements were chosen because, in the case of nickel and cobalt, the atomic weight and atomic number are in reverse order.

CHEMICAL ABSTRACTS.

Crystallisation of a Radium Barium Solution. CLARENCE E. SCHOLL (*J. Amer. Chem. Soc.*, 1920, **42**, 889—896).—Crystallisation of the systems radium chloride–barium chloride and radium bromide–barium bromide are considered theoretically, and a number of experiments based on the theoretical results described. On cooling a saturated solution of the chloride from 100° to 0°, one-half of the total chlorides separates, whilst one-third of the bromides separate under similar conditions. The concentration of radium in any dish in the positive direction is given by $C=AK^n$, where C is the concentration, A the known concentration of the dish at the start, K the factor of enrichment, and n the number of recrystallisations. The concentration of any dish in the negative direction is $C'=A'(X-K)^m/(X-1)^m$, where X is the inverse fractional proportion of the total weight of material occurring as crystals, and m the number of crystallisations in the negative direction. In the case of the chlorides, 50% of the material separates from 0·5N-hydrochloric acid solution, which gives a factor of enrichment of 1·62. Hence $C=A\times1{\cdot}6^n$ and $C'=A\times0{\cdot}4^m$. Crystallising so that the crystals move one dish forward and the liquors two dishes backward, a concentration is effected as follows: if 1·0 be the radium concentration of the starting dish, that of the fifth dish to the right has a concentration of 10·6, whilst the eighth dish to the left has a concentration of 0·026. In the bromide system, one-third the material separates from saturated solutions of 0·33N-hydrobromic acid, and the enrichment factor is 2·49. Hence $C=A\times2{\cdot}49^n$ and $C'=A\times0{\cdot}25^m$. Crystallising so that the crystals go two dishes to the right and the liquors three dishes to the left, the following concentration is obtained. If the radium concentration in the starting dish be 1·0, then the ninth dish to the right has a concentration of 62, and the ninth dish to the left has a concentration of 0·016. Hence the bromide system is more efficient than the chloride system. Several other systems are described.

J. F. S.

Concentration of Radium and Mesothorium by Fractional Crystallisation. JOHN L. NIERMAN (*J. Physical Chem.*, 1920, **24**, 192—200).—A number of crystallisations of barium bromide containing radium bromide and mesothorium bromide have been carried out in neutral solutions and in solutions in hydrobromic acid of various concentrations with the object of ascertaining the conditions under which the optimum crystallisation factor is obtained. By crystallisation factor, the author understands the ratio of radioactive bromide in the crystals to that in the substance before crystallisation. The results show that this factor is independent of the concentration of the hydrobromic acid. The crystallisation factor is given for various percentages of salt separating; thus, when 24·3% of the salt separates, the factor is

2·43, and this decreases with increasing separation to 1·44, when 69·0% separates. For concentrations of mesothorium up to 2 mg. per gram of salt, the crystallisation factor remains constant. The separation of mesothorium and radium from barium can be carried out advantageously in either neutral or dilute acid solutions of the bromides. All measurements of activity were made by means of the γ-ray. J. F. S.

The Conductivity of Permutite Mixtures. V. ROTHMUND and G. KORNFELD (*Zeitsch. anorg. Chem.*, 1920, **111**, 76—77).—Polemical. A reply to A. Günther-Schulze (A., 1919, ii, 490). E. H. R.

Form of the Conductivity Function in Dilute Solutions. Correction. C. A. KRAUS (*J. Amer. Chem. Soc.*, 1920, **42**, 990—991. Compare this vol., ii, 217).—Several of the equations previously published have been corrected. J. F. S.

Electrolytic Potential of the Change Nitrite → Nitrate + Nitric Oxide. The Energetic Relationships of the Most Important Compounds of Nitrogen with Oxygen and Hydrogen. HANS PICK (*Zeitsch. Elektrochem.*, 1920, **26**, 182—196).—A theoretical paper in which it is shown that the normal potential of the change $2NO_2' \longrightarrow NO + NO_3'$ at 25° may be calculated from the electrometric measurements of Moore (A., 1913, ii, 467), and the value +0·49 volt obtained. This value is also obtained from the chemical measurements of the equilibrium of the decomposition of silver nitrite (Abegg and Pick, A., 1906, ii, 833). Using this normal potential, the equilibrium measurements of Lewis and Edgar (A., 1911, ii, 264) for the chemical decomposition of nitrous acid into nitric oxide and nitric acid, the energetic relationships between the substances NO_3', NO_2', NO, and HNO_2 are calculated for 25°, and the results expressed as normal potentials. From thermodynamic relationships and from equilibrium data previously published, the energetic relationships are deduced and expressed as normal potentials for the substances N_2, N_2O, NH_3, $NH_4^{\cdot}$, NO_2, N_2O_4. The normal potentials thus calculated are compared with known chemical and electrochemical data and found to be in good agreement. J. F. S.

Photoelectric Investigations with Salt Solutions. TORSTEN SWENSSON (*Arkiv. Kem. Min. Geol.*, 1917, **7**, No. 19, 1—142).—The change of *E.M.F.* occasioned by illuminating one side of a cell, of the type Pt|soln.||soln.|Pt, by ultra-violet light whilst the other half is dark, has been measured for solutions of potassium and cobalt chlorides, cobalt ammonium sulphate, nickel, cobalt, manganese, chromium, zinc, magnesium, copper, and potassium sulphates, sulphuric acid, hydrochloric acid, mixtures of potassium dichromate and sulphuric acid, potassium ferricyanide and potassium hydroxide, and potassium ferrocyanide, potassium ferricyanide, and potassium hydroxide. All measurements were made

over prolonged intervals, and the solutions were stirred by a fine stream of nitrogen. The measurements were made both with the electrode illuminated and unilluminated. It is shown that in most cases the *E.M.F.* towards an indifferent electrode changes on illumination. The change depends on the nature of the salt, and after the illumination ceases, the *E.M.F.* changes in the direction of the value which the solution previously possessed. Both positive and negative changes of *E.M.F.* are observed, and, in consequence, maxima and minima, as well as inflexion points, are found in the potential–time curves. The theoretical formula

$$E=\rho kLB/(kL+k_1)[1-e^{-(kL+k_1)t}]-\rho k_2L_1B_1/(k_2L_1+k_3)[1-e^{-(k_2L_1+k_3)t}]$$

has been tested by the results obtained with the simple salt solutions and found to be generally obeyed. The nitrogen used is shown to have no other effect than that of a stirrer, and the photoelectrical effect is shown not to be due to the formation of ozone or hydrogen peroxide. The illumination of the electrode is also unnecessary for the production of the potential change. In the case of nickel sulphate, the effect of the light intensity is shown to be in accordance with the formula

$$E=\rho kLB/(kL+k_1)[1-e^{-(kL+k_1)t}].$$

The effect is either proportional to the concentration or entirely independent of the concentration, depending on the relationship between the concentration and the intensity of illumination. Experiments with mixtures of potassium dichromate and sulphuric acid showed that the potential increased on illumination, whilst with the substances alone it decreased. In the mixtures, the effect was at first negative, but soon changed to a strong positive effect. Here also the illumination of the electrode is without effect, and the change of *E.M.F.* is occasioned by the ultra-violet light waves, which are absorbed by glass. The change of *E.M.F.* in these cases is independent of the concentration, but depends on the composition of the mixture, the maximum effect being obtained with a solution containing 75 mols. % of potassium dichromate. The *E.M.F.* returns to the original value when the light is removed with a velocity which depends on the composition of the solution, and is greatest for pure sulphuric acid. Solutions of potassium ferrocyanide in alkaline solution, on illumination showed at first a decreased *E.M.F.*, which rapidly changed to an increased value. In mixtures of ferrocyanide and ferricyanide in alkali, the velocity of the change of potential is greater the larger the amount of ferricyanide present. Experiments with Röntgen rays gave an effect of the same nature, but much smaller than that observed with ultraviolet light. Theories are put forward to explain the effects observed. An historical summary of the work already published on this subject is included in the paper. J. F. S.

The Theory of Electrolytic Ions. XIV. Kohlrausch's Law of Additivity. Richard Lorenz (*Zeitsch. anorg. Chem.*, 1920, **111**, 55—75).—The work of Bjerrum (A., 1919, ii, 9) and

others indicates that strong electrolytes in dilute solution are completely dissociated. The molecular conductivity, μ, can be expressed by the equation $\mu = \alpha F(U+V)$, where α is the degree of dissociation, F the constant of Faraday's law, and U and V the ion mobilities, which are supposed to be invariable. Since the conductivity, μ, with decreasing concentration approaches a limiting value, μ_0, it follows that, if dissociation is already complete, U and V must be variable, and must approach limiting values, U_0 and V_0. A new equation is obtained, $\mu = F(xU_0 + yV_0)$, where x and y are mobility coefficients. According to the old theory, the transport number, n, is given by $n = U/U+V$, and is a constant, independent of the degree of dissociation, α. In terms of the new theory, however, where, instead of variable degree of dissociation, variable ionic mobility is assumed, the transport number also becomes variable, namely, $n = xU_0/(xU_0 + yV_0)$. The transport numbers can only be equal when the mobilities of the two ions (in the case of electrolytes dissociating into two simple ions) are equal, for it is shown that the rate of change of mobility with concentration is the same for all ions. In the cases of potassium chloride, bromide, and iodide, the mobilities of all the ions are approximately equal at the same concentration, and consequently the transport numbers are practically constant for all concentrations. The mobilities and transport numbers of the ions have been recalculated for the salts potassium chloride, bromide, iodide, nitrate, nitrite, chlorate and thiocyanate, and sodium chloride, nitrate and iodate, and the values of the mobility-coefficients of the potassium, sodium, and chlorine ions at different concentrations are tabulated.

E. H. R.

Cadmium-Vapour Arc Lamp. HENRY J. S. SAND (*Phil. Mag.*, 1920, [vi], **39**, 678—679).—An answer to Bates's criticism of the cadmium vapour arc lamp (this vol., ii, 221). The author points out that the difficulties experienced were due in all probability to faulty pumping and to the presence of oxide formed by traces of water vapour.

J. F. S.

Investigation of Mewes' Law of the Relation between the Volume of a Gas and the Temperature. RUDOLF MEWES (*Zeitsch. Sauerstoff Stickstoff Ind.*, 1920, **12**, 10—13; from *Chem. Zentr.*, 1920, i, 694—695).—In continuation of previous investigations (this vol., ii, 227), the author shows that the assumptions underlying the considerations of ideal gases are no longer tenable, and must be replaced by new hypotheses. The experiments, which disprove the older ideas, confirm the equations which have been proposed by him.

Gay-Lussac's law is only valid for nitrogen at the atmospheric pressure, and does not hold for increased or decreased tensions. Conversely, the discrepancies from Mewes's summation law increase greatly with increasing initial pressure. It is found that this phenomenon can be explained by a consideration of the effects of surface condensation and the action of mass. The influence of

surface condensation and partial liquefaction becomes less mark as the tension to which the gases are brought by cooling decrease For this reason, the densities of gases at low temperatures can most accurately estimated by observing the change of tension wi diminishing temperature, as has been demonstrated by a series unpublished experiments. H. W.

Specific Heat of Saturated Vapour and the Entro Temperature Diagrams of certain Fluids. (Sir) J. A. Ew (*Phil. Mag.*, 1920, [vi], **39**, 633—646).—A theoretical paper which the change in the value of the specific heat of a saturat vapour, K_s, with temperature is considered. In the case of stea the value is negative, whilst with ether it is positive. It is show that $K_s = Td\phi_s/dT$, where ϕ_s is the entropy of the saturat vapour, and consequently the value of K_s is negative under conditions that make the entropy of the vapour increase w decreasing temperature. It is negative so long as the entro temperature line for saturated vapour slopes down to the righ this form of curve is found for steam, carbon dioxide, a ammonia, and may be termed the normal curve. If the cur slopes in the opposite direction, the value of K_s is positive, and t type of curve is found for ether, benzene, ethyl propionate, a acetic acid. The entropy–temperature diagrams are drawn fro known data for ethyl alcohol, propyl alcohol, ethyl ether, benze ethyl propionate, and acetic acid. J. F. S.

Specific Heats and Heats of Fusion of the Dichlor Chlorobromo-, Dibromo-, Bromoiodo-, and Di-iod benzenes. Correction. J. Narbutt (*Zeitsch. Elektroche* 1920, **26**, 203—204).—A long list of corrections of formulæ a numerical data which occur incorrectly in the author's papers the above-named subject (A., 1919, ii, 215, 216, 217). J. F. S.

Vapour Pressure and Heat of Vaporisation. J. J. v Laar (*Rec. trav. chim.*, 1920, **39**, 371—410. Compare this v ii, 287).—A theoretical, mathematical discussion of these t physical properties. W. G.

Surface Condensation Error in certain Measureme of Vapour Pressure by the Gas Current Saturation Meth Alan W. C. Menzies (*J. Amer. Chem. Soc.*, 1920, **42**, 978—98 —The condensation of water from its saturated vapour in air on water-washed and steamed glass surface and on an acid-wash steamed, and water-washed asbestos surface has been investigat under the conditions which generally obtain in the use of the g current saturation method of vapour-pressure measurement. the case of glass wool, the condensation amounts to 0·012—0·1 mg. per sq. cm. of glass surface at 22°, whereas asbestos takes about 28—32% of the water from the saturated air. This quanti of deposited water is sufficiently large to explain the many

explained irregularities recorded in the literature of measurements of vapour pressure by this method. J. F. S.

The Manipulation of Volatile Substances. IV. ALFRED STOCK [with ERNST KUSS and KARL SOMIESKI] (*Ber.*, 1920, **53**, [*B*], 751—758. Compare A., 1914, ii, 171; 1917, ii, 442; 1918, ii, 353).—In the estimation of tension in the vacuum apparatus, it should be noted that a certain amount of fractionation occurs in the case of mixtures, whereby the vapour becomes richer than the residue in the volatile constituent. This factor is particularly important when only small quantities of material are available; undue reduction in the size of the apparatus is impracticable, and the experimental results must be interpreted with caution. In estimating the tension of solid substances, it is better to cool the regulating bath to the required temperature or to warm the substance somewhat above the experimental temperature before bringing it into the bath; with the reverse procedure, the temperature only becomes slowly uniform throughout the mass, and the tension registered is that of the coldest portion of the substance.

Fractional distillation is only advantageous in dealing with liquid substances. Solids should therefore be distilled under such pressure that they first liquefy. The receiver should be so cooled that a difference in tension of only a few millimetres exists between the substance under distillation and the distillate. Constant movement of the liquid is advisable, and for this purpose a special apparatus is described and figured; this consists essentially of a small induction coil with a simple interrupted and oscillating core. It is attached to the apparatus in the neighbourhood of the distillation vessel, and keeps the whole apparatus, and therefore the liquid, in steady vibration.

The Gaede rotary mercury-air pump previously used is now replaced by the Volmer mercury vapour pump, a Gaede rotary oil pump being used as accessory, whilst the gases are drawn off by an automatic Töpler pump. An improved automatic valve for use in connexion with the latter is described and figured.

The provision of suitable cooling baths for temperatures slightly above that of liquid air has previously been a matter of difficulty; it is now found that liquid propylene (b. p. -48°) fulfils the required conditions admirably, since it has an extraordinarily low melting point and remains highly mobile at the temperature of liquid air; a disadvantage, however, lies in its gaseous nature at the ordinary temperature. The direct introduction of liquid air into the cooling liquids is to be avoided, on account of the violence of its evaporation and also the unevenness of the induced cooling; the latter drawback is also noticed with baths in which the liquid air is allowed to evaporate in coils immersed in the cooling liquid. A special type of cooling vessel is figured which avoids these disadvantages; the liquid air is brought into a copper cylinder immersed in the cooling bath. Its effect is controlled and uniform, since cooling occurs from above downwards, whilst the metal tends

to equalise the temperature. For extremely low temperatures, th use of a heavy, cylindrical aluminium block is recommended; i this, four holes are bored. One of these serves for the introductio of liquid air, and, to avoid the spurting of the latter, is shielde from the remainder by a vulcanite partition. The remaining hol are used for the insertion of thermometers, substance under i vestigation, etc. The block may be insulated by being suspende in a Dewar vessel. By regulation of the pressure of the air, th temperature of the block may be kept constant to within a fractio of a degree for long periods. Equalisation of temperature betwe the metal and the thermometers, etc., may be hastened by fillin the holes with liquid propylene, but this is only necessary in th case of extremely accurate experiments. The use of aluminium particularly advantageous, since at low temperatures the metal h a low specific heat and an extraordinarily high conductivity fo heat. H. W.

Thermal Capacity of Water between 5° and 50°. W. JAEGER and H. VON STEINWEHR (*Sitzungsber. Preuss. Aka Wiss. Berlin*, 1915, 424—432).—The 15° calorie is found by refine electrical heating measurements to be equivalent to 4·184 inte national watt-seconds. The minimum specific heat of water occu at 33·5°. J. R. P.

The Properties of Fluids in the Neighbourhood of th Critical Point and the Characteristic Equations. G. BRUH (*Compt. rend.*, 1920, **170**, 1173—1175).—A mathematical di cussion of the subject, with special reference to the equations van der Waals and Clausius. W. G.

Absolute Entropies of Monatomic Substances. MAX PLAN (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1916, 653—667).—Fro the equations of statistical mechanics, the characteristic therm dynamic functions are derived for a single atom moving freely a hollow sphere and in a hollow, rectangular parallelopiped. Th calculation is then extended to a monatomic gas, and it is show that the degrees of freedom corresponding with the separate ato must be incoherent. The expression of Nernst (*Verh. Deu Physikal. Ges.*, 1916, **18**, 83) for the energy of a gas is disco tinuous in respect of temperature, so that a definite value of t specific heat cannot be found. Those deduced by Stern and Tetro are identical with that found in the present paper, with t exception of an additive constant. J. R. P.

Relationships between Critical Data and other Properti of Organic Liquids. W. HERZ (*Zeitsch. anorg. Chem.*, 19 **111**, 52—54. Compare A., 1920, ii, 285).—It has been show that, for a large number of non-associated organic compounds, t quotient of the critical temperature, T_k, and the critical pressu p_k, divided by the sum of the valencies of the constituent ato (C=4, H=1, O=2, and N=3), is approximately a constant, 0·4

From the known relationship between critical volume, temperature, and pressure, it follows that $v_k/z=$const., where v_k is the critical volume and z the sum of the valencies. This is shown to be the case for a number of esters, ethers, and hydrocarbons, the value of the constant varying between 0·00038 and 0·00047. It is also deduced that the value of the heat of vaporisation, L, can be found from the expression $L=T_s/0{\cdot}45d_kz$, where T_s is the boiling temperature (abs.) and d_k the critical density. The molecular refraction, $MR=1{\cdot}8T_k/p_k$, can be written $MR=0{\cdot}8z$. Since, however, the molecular refraction depends also on the constitution of the compound, the values calculated from the formula are only approximate. E. H. R.

Comparative Method for Determining Vapour Densities. PHILIP BLACKMAN (*J. Physical Chem.*, 1920, **24**, 225—229).—Two glass bulbs made of graduated burette tubing and about 10 cm. long are joined together by capillary tubing. The free ends are narrowed and drawn out into tubes of sufficient diameter to admit small weighing tubes. The apparatus is placed upright and half illed with mercury. The substances the vapour densities of which are to be compared are weighed out in very small quantities (0·02—0·10 gram) in narrow glass tubes and placed one in each bulb. One of the bulbs is then sealed at the top, and, when cooled o a known temperature, the difference in the height of the mercury evels is noted and the positions of the mercury level also noted, so hat later the volume of air (V) in the sealed bulb may be determined. The other bulb is then sealed, and the same measurements of mercury levels again taken, so that the volume of air (V_1) may be determined. The apparatus is now placed in a deep beaker, covered with a suitable liquid, and heated to a temperature ufficiently high to vaporise completely both liquids. Again the mercury levels are determined, so that v_1 and v_2, the volume of air and vapour in the two tubes, may be determined. The apparatus is now inverted, and the graduated tube cut away from he horizontal connecting tube, and the volumes, V, V_1, v_1, and v_2, determined by filling with mercury from an accurate burette o the observed levels. Four approximate formulæ for calculating he vapour density are given, which are applied to measurements with acetone, diethyl ether, chloroform, and ethyl alcohol. The esults are very good. J. F. S.

Some Consequences of the so-called Deterioration Theory of Gases. W. NERNST (*Sitzungsber. Preuss. Akad. Wiss., Berlin*, 919, 118—127).—At very low temperatures, the ordinary gas law, $pv=RT$, is replaced by the equation $p=(R/V).\beta\nu/(1-e^{-\beta\nu/T})$, where $\beta=4{\cdot}863.10^{-11}$; $\nu=hN^{\frac{2}{3}}/4\pi mV^{\frac{2}{3}}$, where $N=6{\cdot}17.10^{23}$, $h=6{\cdot}55.10^{-27}$, $m=$mass of molecule. For $T=0$, this leads to a ressure at the absolute zero, $p=h^2N^{\frac{2}{3}}/4\pi mV$. This pressure is ssumed to be due to directed repulsive forces analogous to valency cting between the molecules, which are inversely proportional to

the cubes of the distances. These will be appreciable only a extremely small distances, that is, at very low temperatures. Th theory leads to the following equation for the viscosity at very lov temperatures, $\eta = m^3u^3/9h^2$, where u is the molecular velocity. Th connexiou between viscosity and temperature required by th theory is approximately fulfilled by the measurements on hydroge at the lowest temperatures. The result is an indirect confirmatio of the "deterioration theory" proposed by the author. J. R. P.

Compressibility and Viscosity of Water and of it Solutions, and its Polymerisation. STEFANO PAGLIANI (*Gazzetta* 1920, **50**, i, 186—194).—The author discusses the work of Richard and Palitzsch (A., 1919, ii, 97), Pagliani and Palazzo (*Atti R Accad. Sci. Torino*, 1884, **19**), Pagliani and Vicentini (*Mem Accad. Lincei*, 1884, **19**), Pagliani (*Rend. R. Accad. Lincei*, 1889 **5**), Tait (*Proc. Roy. Soc. Edin.*, 1882, **12**), Tammann (A., 1910 ii, 495), van Laar (A., 1900, ii, 189), Bousfield and Lowry (A. 1910, ii, 842), Battelli (*Atti R. Accad. Sci. Torino*, 1885, **20**), an Pagliani and Oddone (*Atti R. Accad. Sci. Torino*, 1887, **112**), an draws the conclusion that the hypothesis of the polymerisation o water serves to explain most of the observations made on wate and aqueous solutions with reference to their compressibility an viscosity, and to the variations of these with change of temperature pressure, and concentration of the solutions. T. H. P.

The Viscosity of Colloidal Solutions. PAUL BARY (*Compt rend.*, 1920, **170**, 1388—1390).—If a unit volume of dry colloic is swollen hy a volume, a, of liquid, Einstein's formula for th viscosity may be written $a = (\eta - 1 - 2{\cdot}5v_0)/2{\cdot}5v_0$, where η is th viscosity of the colloidal solution, that of the pure medium bein taken as unity, and v_0 is the amonnt of colloid in unit volume This gives a means of determining the coefficient of swelling by viscosity measurements. It is shown that colloids which enter int suspension in a given medium without any external agency yiel liquids in which the colloid shrinks progressively with the tim to a degree which depends on the concentration and the tempera ture. This shrinking is accentuated by dilution, and tend towards zero for zero concentration. W. G.

Adsorption of Hydrogen by Quartz at Low Temperatures G. R. PARANJPE (*Proc. Asiatic Soc. Bengal*, 1919, **15**, cxxxvi—cxxxvii).—An apparatus based on the principle of the differentia manometer was used. Differences in pressure due to unequa adsorption in the two bulbs were measured by the volume chang necessary to re-establish equilibrium. The measurements wer made at −190° and at pressures from 25 to 350 mm. The volume of hydrogen adsorbed at these pressures by 100 sq. cm. of quart surface, corrected to normal temperature and pressure, wer 2·0 c. mm. and 10·5 c. mm. respectively. The results were use in calculating the correction for a hydrogen thermometer of quartz

Even at this low temperature the correction is very small. Work with other gases and at other temperatures is in progress.

CHEMICAL ABSTRACTS.

Adsorption of Sulphur Dioxide by the Gel of Silicic Acid. JOHN MCGAVACK, jun., and W. A. PATRICK (*J. Amer. Chem. Soc.*, 1920, **42**, 946—978).—The adsorption of sulphur dioxide by silicic acid gels has been measured at 100°, 80°, 57°, 40°, 30°, 0°, −33·4°, −54°, and −80°. The effect of the water content of the gel was determined by using gels containing 2·31, 3·51, 4·86, and 7·97% of water respectively. It is shown that the maximum adsorption is exhibited by gels containing about 7% of water. The adsorption is shown to be reversible in all cases in the absence of air. In the presence of small amounts of air, the rate of adsorption was greatly decreased, and adsorption and desorption were irreversible. The empirical equation of Freundlich was found to hold over almost the entire range studied, exceptions being at those points where the saturation pressure was approached. The equation $V/\sigma^{1/n} = K(p/p_0)^{1/n}$ is found to hold, where V is the uncorrected volume of the condensed phase, σ the surface tension, p the pressure of the gas phase, p_0 the vapour pressure of the liquid, and K and $1/n$ constants dependent on the physical properties of the adsorbent. J. F. S.

Sorption of Vapours by Charcoal. BROR GUSTAFSON (*Arkiv. Kem. Min. Geol.*, 1917, **7**, No. 22, 1—17).—The sorption of vapours of water and acetic acid by charcoal has been examined at a series of pressures (4·6—17·4 mm.) and at temperatures 16·5—20°. In the case of water vapour, it is shown that for small pressures the amount of sorption is proportional to the pressure, and the sorption in these cases must consist in the formation of a solid solution; at pressures from 6—7 mm., the strict absorption commences. On producing the solution and absorption curves, they cut at a pressure 7·4 mm. The sorption velocity is greatest at the commencement, and decreases as the equilibrium conditions are approached; it is also greater at the lower pressures than at the higher pressures. In the case of acetic acid, much the same results are observed, but here an hysteresis occurs. The saturation pressure is greater when reached from above than when reached from below. This is held to be due to the two processes, solution and absorption, occurring simultaneously. J. F. S.

Electrolytic Conductivity in Non-aqueous Solutions. IV. The Solvation of the Ions of *p*-Tolyltrimethylammonium Iodide in a Number of Organic Solvents. HENRY JERMAIN MAUDE CREIGHTON (*J. Franklin Inst.*, 1920, [5], **189**, 641—643. Compare A., 1919, ii, 44).—Walden's formula (this vol., ii, 230) is used to calculate the solvation of the ions of *p*-tolyltrimethylammonium iodide in a number of solvents. The molecular weight of the solute will be increased above the normal value, corresponding with Walden's equation, if solvation occurs. The solvation

values obtained with the solvents were: propaldehyde, 7·73; epichlorohydrin, 3·44; ethyl alcohol, 3·30; methyl alcohol, 2·91; benzaldehyde, 2·88; anisaldehyde, 2·21; propionitrile, 1·44; acetone, 1·29; nitromethane, 0; benzonitrile, 0; nitrobenzene, 0. Since Walden has shown that the iodide ion is not solvated in methyl alcohol, ethyl alcohol, acetone, and nitrobenzene, the above values probably represent the degrees of solvation of the organic cation. *The tendency to solvation in aldehydes decreases with increase in* the molecular weights of the latter. J. R. P.

Tabulation of Hydrogen- and Hydroxyl-ion Concentrations of some Acids and Bases. ARTHUR W. THOMAS (*J. Amer. Leather Chem. Assoc.*, 1920, **15**, 133—146).—The hydrogen-ion concentrations of the following acids are given for concentrations from 0·001*M* to 2*M*: acetic, boric, butyric, carbonic, citric, formic, gallic, hydrochloric, lactic, nitric, oxalic, phosphoric, salicylic, sulphuric, and tartaric. The hydroxyl-ion concentrations of ammonium, barium, calcium, potassium, and sodium hydroxides are also given. The values for the weak acids were calculated from Ostwald's dilution law, and for the strong acids from curves constructed from data in the literature. CHEMICAL ABSTRACTS.

Surface Energy of Crystals and its Influence on the Crystalline Form. M. BORN and O. STERN (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 901—913).—A mathematical paper in which the surface energy of a crystal in a vacuum is calculated from the electrostatic forces between the ions. J. R. P.

Anisotropic Liquids. I. M. BORN (*Sitzungsber. Preuss. Akad. Wiss., Berlin*, 1916, 614—650).—The theory that the molecules of anisotropic liquids are elongated in the direction of one axis, and that the orientations between the axes depend on the temperature, according to a law of distribution, is completed by the calculation of the law of distribution, on the assumption that the molecules are electrical dipoles, and that the directive forces are purely electrical. The liquid crystal is then analogous to the magnet considered in the theory of Langevin and Weiss. The Curie point of a magnet corresponds approximately with the transition point between anisotropic and isotropic states. From the known transition points of anisotropic liquids, the electric moments of the dipoles are calculated. The optical properties of the substances are also calculated, and found in qualitative agreement with experiment. A liquid composed of dipoles will exhibit double refraction in an electric field at sufficiently high temperatures; the expression for Kerr's constant deduced on this theory is similar to that found by Langevin in another manner. J. R. P.

Anisotropic Liquids. II. Dependence of the Refractive Index at Right Angles to the Optic-axis on the Temperature. M. BORN and F. STUMPF (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1916, 1043—1060).—Measurements of the change of refractive

index with temperature made with anisotropic liquids confirm the theory advanced by one of the authors (see previous abstract).

J. R. P.

An Altered Formulation of the Quantum Hypothesis. M. PLANCK (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1914, 918—923).—The expression for the energy of a resonator derived from the quantum hypothesis may be obtained on the assumptions that: (1) the exchange of energy between resonators and radiation is continuous, instead of quantum emission and continuous absorption postulated in a previous hypothesis; (2) exchange of energy between resonators and free particles (molecules, ions, and electrons) occurs in quanta. The formulæ of the classical electrodynamics then apply to the reciprocal action between resonators and radiation, and many former difficulties are removed. In the collision of a free particle with a resonator, it is assumed that the latter gives up the whole of its energy to the particle, whilst the particle imparts to the resonator amounts of energy which are whole multiples of the quantum. The free particles in solids may be vapour molecules, since the number required is so small as not to contribute materially to the specific heat of the solid. J. R. P.

Variance and the means of Presuming its Value without the Aid of any Formula. C. RAVEAU (*Compt. rend.*, 1920, **170**, 1385—1387).—A theoretical discussion of the variance of systems, certain systems being discussed and their variance arrived at without calculation. W. G.

Equilibrium between Chlorine, Water, Hydrochloric Acid, and Chloric Acid. Free Energy of the Chlorate Ion. AXEL R. OLSON (*J. Amer. Chem. Soc.*, 1920, **42**, 896—904).—The equilibrium constant of the reaction $3H_2O + 3Cl_2 = HClO_3 + 5HCl$ has been experimentally determined at 91°. The reaction mixture was sealed in glass tubes with a little ($0{\cdot}02M$) manganous chloride, which acted as a catalyst. Equilibrium was slowly reached from both sides, and by means of the equation

$$K' = (H^{\cdot})^6 \times (Cl')^5 \times (ClO_3')/(Cl_2)^3$$

the equilibrium constant is calculated to 10×10^{-6}. The free energy of the reaction $3Cl_2(aq.) + 3H_2O(liq.) = 6H^{\cdot} + 5Cl' + ClO_3'$ is 10,600 cal. at 91°, and at 15° it is 6640 cal. The free energy of formation of the chlorate ion is given from the equation $0{\cdot}5Cl_2(gas) + 1{\cdot}5O_2 + \ominus = ClO_3'$, for which $\Delta F_{298} = -1374$.

J. F. S.

Registration of Rapid Pressure Changes. W. NERNST (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1915, 896—901).—The behaviour of vibrating membranes used in pressure measurements during gaseous explosions is considered mathematically. The rise of pressure during explosion in a closed vessel is stated to follow the law, $p = p_0(1 - e^{-at})$, where p_0 is the maximum pressure, t is the time, and a is a constant. The main results, however, are

independent of this special hypothesis. Of the two solutions of the equation, only one has been realised with gaseous explosions, namely, the execution by the registering membrane of vibrations of small amplitude about the position corresponding with the instantaneous pressure. The other solution may be represented by high explosives of the "brisant" type. Great disturbances in the motion of the membrane may occur when wave motion is set up in the gas. J. R. P.

The Use of Conductometric Titrations in Neutralisation Analysis. I. The Neutralisation of Acids and Bases. I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, **111**, 1—27).—The object of the experiments was to investigate the relationship between the neutralisation curve on the one hand and the dissociation constants and dilution on the other. The experiments were conducted by titrating a dilute acid solution with a relatively strong solution of the base, so that the dilution of the liquid of which the conductivity was being determined was not appreciably changed during the titration. The neutralisation curve was obtained by plotting the relative conductivities as ordinates against the quantities of alkali added as abscissæ. When a strong acid is neutralised by a strong base, the neutralisation curve falls steeply as a straight line to the neutral point, and then rises steeply as the alkalinity increases. Up to the neutral point, the neutralisation curve is the resultant sum of the acid conductivity curve and the salt conductivity curve. By titrating a solution of the salt into pure water, a curve is obtained, the salt conductivity curve, which cuts the neutralisation curve at the neutral point. The sharpness of the neutral point is independent of the mobility of the anion, but the point becomes less distinct on the neutralisation curve the greater the mobility of the cation.

When an acid of medium strength, such as salicylic acid, is neutralised by a strong base, the neutralisation curve has a concave form and passes through a minimum before the neutral point is reached. Beyond the neutral point, the curve rises sharply as a straight line, but the neutral point is not distinct. It can, however, be found by determining the conductivity curve of the salt, since the salt curve cuts the neutralisation curve in the neutral point. The conductivity of the unneutralised acid at any stage of the neutralisation can be deduced from the neutralisation curve and the salt conductivity curve, or it can be calculated from the ion mobilities. From the "acid depression curve" so obtained, the dissociation constant of the acid can be calculated. To obtain good titration results at dilutions 0·1, 0·01, 0·001*N*, the dissociation constant of the acid should be less than 5×10^{-4}, 5×10^{-5}, or 5×10^{-6} respectively.

In the titration of a very weak acid with a strong base, the neutralisation curve may, from the start, correspond practically with the salt curve up to the neutral point; if the acid is very weak and the salt highly hydrolysed, it is impossible to determine the nentral point. The dissociation constant of the acid must be

ot less than 10^{-10} for a $0{\cdot}1N$-solution or 10^{-9} for a $0{\cdot}01N$-solution o obtain good results. Boric acid ($K=6{\cdot}6\times10^{-10}$) and phenol $K=10^{-10}$) were successfully titrated with sodium hydroxide. Veak acids and weak bases can be titrated if their dissociation onstants are greater than 3×10^{-6}. Thus acetic acid can be trated with ammonia, but boric acid cannot, because, on account f the hydrolysis of the neutral salt, the whole neutralisation curve s rounded off, and there is no sharp change of direction at the eutral point. E. H. R.

The Use of Conductometric Titrations in Neutralisation Analysis. II. The Simultaneous Titration of Different Acids or Bases. I. M. Kolthoff (*Zeitsch. anorg. Chem.*, 1920, **111**, 28—51. Compare preceding abstract).—When a strong and a weak acid are titrated together, the acid conductivity curve falls at first along a straight line. If, when the stronger acid is nearly neutralised, the conductivity of the weaker acid is not negligible, the point of neutralisation of the strong acid is not sharp on the neutralisation curve. It can, however, be found by plotting the conductivity curve of the salt of the strong acid, and finding the point of intersection of this straight line with the first, straight portion of the neutralisation curve. In this way, hydrochloric acid can be titrated, for example, in presence of formic acid. The point of neutralisation of the formic acid is given sharply by the change of direction of the curve when the solution becomes alkaline. To get good results, when titrating $0{\cdot}1N$-solutions of the two acids in equal concentrations, the dissociation constant of the weaker acid should be less than 4×10^{-4}. Addition of alcohol, which tends to suppress the dissociation of the weak acid, is sometimes advantageous.

Two weak acids can be titrated together in equal concentrations when the ratio of their dissociation constants is smaller than 0·001, but if the concentration of the weaker acid is ten times that of the stronger, the ratio must be smaller than 0·0001. Since, however, the sharpness of the result depends on the magnitude of the angle of intersection of the two straight lines representing the two portions of the neutralisation curve, and the change of direction of the curve depends on the relative mobilities of the anions of the two acids, it follows that the accuracy of the result depends on the mobilities of the anions, and if these are approximately equal, no definite result can be obtained. Thus oxalic acid and tartaric acid, or oxalic acid and phenol, can be titrated together, but not acetic acid and phenol. When a dibasic acid is titrated, the first and second equivalent points can only be found if the two dissociation constants are markedly different. This occurs in the case of oxalic acid. In the case of tartaric acid, the first equivalent point is not sharp even in presence of alcohol, and in the case of succinic acid it cannot be determined at all.

Two weak acids with approximately equal dissociation constants cannot be titrated together, but if the dissociation constants and ion mobilities are known, the composition can be calculated from

the conductivity of the mixture. A fresh determination of the dissociation constant of formic acid gave $2{\cdot}05 \times 10^{-4}$ at 18°.

The same considerations apply to the titration of mixtures of bases as to mixtures of acids. E. H. R.

Catalysis of Oxy-hydrogen Gas by Palladium Mixed Crystals. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1920, **111**, 90—96).—Experiments were made with palladium–silver and palladium–gold alloys, containing from 0 to 100% silver and gold respectively, to determine the influence of the composition of the metal on the temperature at which catalysis of a hydrogen–oxygen mixture (prepared by electrolysis of sodium hydroxide solution) commences and, on cooling, ceases. The observed temperature at which catalysis ceases is generally considerably lower than that at which it commences, because, during cooling, the heat of reaction tends to keep the temperature of the contact surface between catalyst and gas above that of the surroundings. The form of the catalyst also influences the limiting temperatures; for these experiments, the metal was in the form of thin wire wound into a close spiral. With pure palladium, catalysis started at 145—163° and ceased at 35—50°. In the palladium–silver series, both limiting temperatures rose slowly until the proportion of silver reached 80%, when there was a sudden rise to 370—380° (starting temperature) and 270—276° (cessation of catalysis). In the palladium–gold series, there was little change up to 70% gold, then a rapid rise of the limiting temperatures over the range from 70% to 100% gold. There appears to be a close connexion between the velocity of solution of hydrogen in the catalyst and the rate of catalysis. In the palladium–silver series between 200° and 300°, the solubility of hydrogen is very slight in the alloy containing 70—80% silver, and the same is true of the 80% gold alloy in the palladium–gold series. These compositions correspond with the rapid rise observed in the limiting temperatnre of catalysis. The rate of catalysis probably depends, however, not so much on the actual solubility of hydrogen as on its rate of solution in the catalyst. E. H. R.

Acceleration of the Decomposition of Hydrogen Peroxide by Colloidal Rhodium. C. ZENGHELIS and B. PAPACONSTANTINOS (*Compt. rend.*, 1920, **170**, 1178—1180. Compare this vol., ii, 380).—The decomposition of hydrogen peroxide by a colloidal solution of rhodium is a unimolecular reaction, the velocity of which is considerably accelerated by previously bubbling either hydrogen or carbon monoxide through the colloidal solution. W. G.

Catalytic Actions at Solid Surfaces. III. Hydrogenation of Acetaldehyde and the Dehydrogenation of Ethyl Alcohol in the Presence of Finely Divided Metals. E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 259—264. Compare A., 1919, ii, 403; this vol., ii, 102).—The hydrogenation of acetaldehyde and the dehydrogenation of ethyl alcohol in the presence of metallic nickel and copper have been investigated at

temperatures 120—300°. It is shown that acetaldehyde is converted into ethyl alcohol by hydrogen under these conditions, in the case of copper at 200° the yield of alcohol being 87·6%; in the case of nickel, the aldehyde has a tendency to break up into carbon monoxide and methane. In the dehydrogenation of alcohol in the presence of copper, a yield of 90—95% of acetaldehyde may be obtained at 295—300°. In the dehydrogenation of alcohol, the presence of water improves the yield of acetaldehyde relatively to that of hydrogen. *There are always small quantities of by-products, notably n-butaldehyde, crotonaldehyde, and ethyl acetate, the total amount of which is normally 1—2%.* The presence of *a small proportion of water protects acetaldehyde from hydrogenation, and in some cases prevents the action entirely. The primary action of the catalyst in all these cases is to effect an association with the carbon compound, the resulting unstable complex then being resolved into other compounds.* J. F. S.

Catalytic Actions at Solid Surfaces. IV. Interaction of Carbon Monoxide and Steam as Conditioned by Iron Oxide and by Copper. E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 265—273. Compare preceding abstract). —The reaction $CO + H_2O \rightleftharpoons CO_2 + H_2 + 10{,}200$ cal. has been studied, using both ferric oxide and copper as contact substances. The reaction has been carried out using 95% carbon monoxide and using water-gas containing 40% carbon monoxide at temperatures from 227° to 600°. It is shown that copper is much less complete in its action than iron oxide at the higher temperatures, but over the range 200—300° it is definitely more active than iron oxide. Copper commences to act at a reasonable rate at about 220°, whereas iron oxide is barely active at 250°, and does not reach full activity until about 400°. On passing water-gas (5·1% carbon dioxide, 39·9% carbon monoxide, and 47·3% hydrogen) with steam in the presence of ammonia through a tube at 350°, sufficient ammonium formate was obtained for purposes of identification. The relative activities of copper and iron oxide toward carbon monoxide and steam at the lower ranges of temperature are closely parallel to their respective powers of decomposing formic acid and steam. The amount of action effected by the copper catalyst declines somewhat after 350°, and the maximum change effected appears to be greater the higher the proportion of carbon monoxide in the gas. J. F. S.

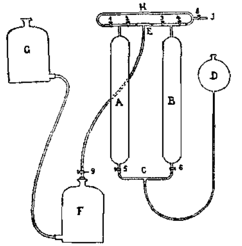
Heat of Dissociation of Hydrogen according to the Bohr–Debye Atom Model. M. PLANCK (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 914—931).—The heat of dissociation of a hydrogen molecule is, at sufficiently low temperatures, equal to the difference between the energy of the two atoms and that of the molecule. On the first assumption, that in all the atoms and all the molecules of hydrogen the electrons describe circular orbits with single quanta, the heat of dissociation is found to be 62,100 cal. The actual value is higher, probably in the region of

100,000 cal. On the second assumption, that in all the atoms and all the molecules those electronic orbits which possess less than one quantum are correspondingly probable, the heat of dissociation is found by classical mechanics to be infinite; on the theory of relativity it would be 570.000 cal., which is certainly too high. The value 140,000 cal., in much better agreement, is obtained on the assumption that, in addition to circular orbits, the electrons may perform pendulum oscillations. It is concluded that the arbitrary assumption of circular orbits made by Bohr is not justified. J. R. P.

The Absolute Calculation of Crystal Properties from Bohr's Model Atom. M. Born and A. Landé (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1918, 1048—1068).—A mathematical paper in which the positions of the atoms in a cubic space-lattice are deduced from Bohr's model of the atom. J. R. P.

Metals. I. and II. F. Haber (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 506—518. 990—1007).—I. The elastic properties and photoelectric effect are discussed on the hypothesis that a metal consists of a space-lattice of positive ions and free electrons. II. The energies of salts, heats of hydration of ions, the Volta effect, etc., are calculated. J. R. P.

Apparatus for Measuring [and Circulating] Gases Soluble in Water. Bernhard Neumann and Heinrich Schneider (*Zeitsch. angew. Chem.*, 1920, **33**, 128).—An apparatus suitable for measuring and circulating small quantities of gas, soluble in water, consists essentially of two pipette-shaped glass vessels, *A* and *B*, provided at the upper ends with T-pieces having stop-cocks, 1, 2, 3, 4, and terminating below in stop-cocks, 5, 6, the latter being connected by a T-piece, *C*, and in communication with a levelling vessel, *D*. The top T-pieces are connected by another T-piece, *E*, as well as by a bent tube, *H*, with a lateral branch, *J*, provided with a stopcock, 8, and leading to the gas reaction vessel or other apparatus. *E* is connected by tubing to a gas collector, *F*, with a three-way tap, 9, and *G* is a pressure vessel for controlling the movement of gas in *F*.



A and *B* are first half filled with water saturated with the gas. By suitable manipulation of the stopcocks, gas is introduced into *A*, and the air is expelled through *B*, after which gas is introduced into *B*, the whole apparatus now being filled with gas, and further solution by the

water being prevented. The gas may be circulated through both vessels or retained in either for measurement under atmospheric pressure. W. J. W.

Inorganic Chemistry.

Improved Kipp's Apparatus for the Preparation of Chemically Pure Hydrogen in the Laboratory. M. DOLCH (*Chem. Zeit.*, 1920, **44**, 378).—The gas delivery tube from the central bulb of a Kipp's apparatus is connected by a three-way cock and side-tube to a stopper and three-way cock in the mouth of the top globe, which is also connected through a second tube to a mercury trap. Pure stick zinc is used in the central bulb, and the apparatus is filled with pure hydrogen before the introduction of air-free dilute sulphuric acid. The space above the acid in the top bulb, being connected to the generator bulb, is always filled with hydrogen, which can be drawn off at will from either bulb by suitably placing the three-way cocks. Excess of pressure is released through the mercury trap. E. H. R.

Triatomic Hydrogen. GERALD L. WENDT and ROBERT S. LANDAUER (*J. Amer. Chem. Soc.*, 1920, **42**, 930—945).—A reactive modification of hydrogen has been produced by several methods, all of which are dependent on gaseous ionisation: (i) by the α-rays from radium emanation, (ii) by an electrical discharge under reduced pressure, and (iii) by the high potential corona at atmospheric pressure. Attempts to produce activation by Schumann light rays failed. This active hydrogen reduces sulphur, arsenic, phosphorus, mercury, nitrogen, and both acid and alkaline solutions of potassium permanganate. It is condensed or destroyed by temperatures about that of liquid air. It is very unstable, and reverts to the ordinary form in about a minute. It passes readily through glass wool, and is not less stable at atmospheric pressure than at low pressures. The activity is not due to gaseous ions, and the properties of the gas are quite different from those of Langmuir's atomic hydrogen (A., 1912, ii, 826, 1162; 1914, ii, 104; 1915, ii, 249). The formation of a polyatomic molecule is indicated by the contraction of the hydrogen when ionised. Positive ray analysis at very low pressures shows a large proportion of triatomic molecules, which are undoubtedly the molecules responsible for the chemical activity. All the properties of the gas point to it being an ozone form, perhaps, properly called "*hyzone*." The existence of triatomic hydrogen is applied to the explanation of Lind's "cluster ion" hypothesis (A., 1912, ii, 513). The calculations of Bohr, based on the Rutherford atom, furnish the only valency hypothesis which satisfactorily accounts for the existence of triatomic hydrogen. J. F. S.

Chemical Decomposition of Hydrogen Peroxide. CHR. WINTHER (*Danske Vid. Selsk. Math. Phys. Medd.*, 1920, **2**, No. 1, 1–18; from *Chem. Zentr.*, 1920, i, 723).—The author confirms Kistiakowsky's observation that the decomposition of hydrogen peroxide in light is notably catalysed by the presence of potassium ferrocyanide. When dilute mixed solutions are placed in ultraviolet light, decomposition ensues very slowly at first, subsequently more rapidly, and finally attains a constant rate; the phenomenon is explained by the assumption of the gradual formation of an extremely stable substance which catalytically accelerates the decomposition of hydrogen peroxide. H. W.

The Behaviour of Non-metallic Hydrides towards Chlorine. ALFRED STOCK [with ROBERT WINTGEN] (*Ber.*, 1920, **53**, [*B*], 837—842).—The experiments recorded in the literature of this subject are concerned for the most part with the products obtained by rather drastic action. The author gives an extended review of the available data, and describes a series of experiments, some of them of a preliminary nature, on the regulated action of the halogen, the experiments being performed at low temperature and frequently in the presence of an inert solvent, such as liquid hydrogen chloride. In spite of certain gaps in the evidence, the following statements may be made. Only five non-metals yield partly chlorinated hydrides which are stable at the ordinary temperature, B_2H_5Cl, CH_3Cl, SiH_3Cl, CH_2Cl_2, SiH_2Cl_2, $CHCl_3$, $SiHCl_3$, NH_2Cl, ($NHCl_2$?), OHCl. Amongst these, the compounds of boron, nitrogen, and oxygen are most unstable, whilst chloromonosilane is more readily decomposed than methyl chloride, a close dependence on the position of the element in the periodic system being observable. The maximum stability is observed with carbon, and is attributable to the equality in the affinity of this element for positive and negative groups. The stability of the partly chlorinated hydrides diminishes in all directions from carbon. The compounds exhibit a more or less strongly marked tendency to decompose into the pure hydride and pure chloride (for example, B_2H_5Cl into B_2H_6 and BCl_3). In the nitrogen group (N,P,As,Sb), in which the instability of the partly chlorinated hydride increases with increasing atomic weight of the nuclear element, reaction immediately occurs, either with the initial hydride or by further action of the initial decomposition products among themselves, whereby hydrogen chloride is eliminated, and either condensed hydrides relatively poorer in hydrogen (N_2H_4,P_2H_4; that is, $NH_2Cl + NH_3 = N_2H_4 + HCl$) or the free elements (that is, $AsCl_3 + AsH_3 = 2As + 3HCl$) are formed. The former frequently are further converted into solid hydrides still poorer in hydrogen ($P_{12}H_6$,P_9H_2,AsH[?]). In the oxygen group, the ability to form a partly chlorinated hydride is only observed in the element of smallest atomic weight, oxygen itself (OHCl). In this compound the tendency towards decomposition into hydride and chloride is still observable ($2OHCl = OH_2 + OCl_2$), but the change to hydrogen

chloride and oxygen is more characteristic. Correspondingly, the action of chlorine on the remaining hydrides of the oxygen group leads exclusively to the formation of the free elements, S, Se, Te.

H. W.

Electrolysis of Hydrogen Bromide in Liquid Sulphur Dioxide. LANCELOT SALISBURY BAGSTER and GEORGE COOLING (T., 1920, **117**, 693—696).

Bromine Chloride: its Combination with Ethylene. MARCEL DELÉPINE and LUCIEN VILLE (*Compt. rend.*, 1920, **170**, 1390—1392).—Although physical chemists deny the existence of a bromine chloride, the authors consider that the behaviour of a solution of chlorine in bromine towards ethylene, the main product being chlorobromoethane, is strong evidence in favour of the existence of such a compound. W. G.

The Photochemical Oxidation of Hydrogen Iodide. CHR. WINTHER (*Danske Vid. Selsk. Math. Phys. Medd.*, 1920, **2**, No. 2, 1—28; from *Chem. Zentr.*, 1920, i, 723—724).—Thin, rapidly moved layers of hydrogen iodide solution, when subjected to the conjoint action of oxygen at a constant pressure and light, are oxidised very slowly initially, then more rapidly until the process attains a constant velocity. The phenomenon is due to the autosensitising action of the liberated iodine. Similar action is observed in the cases of the photochemical oxidation of the leuco-bases of certain dyes (Gros, 1901), of alkaline solutions of pyrogallol (Trautz and Thomas, 1908), and of aqueous sodium sulphite solution (Trautz, 1909). In each instance, a slow oxidation at any rate must be assumed to occur in the dark. H. W.

The Estimation of the Density of Oxygen according to Dewar and Kamerlingh Onnes. RUDOLF MEWES (*Zeitsch. Sauerstoff Stickstoff Ind.*, 1920, **12**, 14; from *Chem. Zentr.*, 1920, i, 664).—The data obtained by Dewar in 1902 and by Onnes in 1911 for the vapour density of oxygen are in good agreement at $-182°$ with Gay-Lussac's law, although the latter is known not to hold at such low temperatures. The author now shows that the values for the apparent alteration in volume are in accordance with the law, but that such values are not in reality the data which are to be determined; after applying the necessary corrections, much lower results are obtained. H. W.

Rutherford's Experiments on the Subdivision of the Nitrogen Nucleus. W. LENZ (*Naturwiss.*, 1920, **8**, 181—186; from *Chem. Zentr.*, 1920, i, 768).—The theory of relativity, according to which mass is connected with every energy, throws light on the questions of simple numbers for atomic weights and of the stability of nuclei. From this point of view, the stability of the helium nucleus is readily understood, whilst the instability of the nitrogen nucleus is explicable. The author considers the persistent oxygen radiations to be possibly helium α-rays. H. W.

Action of Nitrous Acid on Coloured Indicators. C. MATIGNON and G. GIRE (*Bull. Soc. chim.*, 1920, [iv], **27**, 362—366). —A mixture of nitric and nitrous acids was titrated with $N/10$-sodium hydroxide, *different indicators being used for the different titrations*. Of the indicators used, only sodium ferric salicylate characterised the nitrous acid, and this was not sharp. Thus nitrous acid, contrary to the conclusions derived from the heats of neutralisation, is a much stronger acid than the second acid function of phosphoric acid. This is borne out by a study, by electrical conductivity measurements, of the progressive displacement of nitrous acid by sulphuric acid in a dilute solution of sodium nitrite.
W. G.

Production of Concentrated Nitric Acid from Nitrous Gases. F. FOERSTER, TH. BURCHARDT, and E. FRICKE (*Zeitsch. angew. Chem.*, 1920, **33**, 113—117, 122—127, 129—132).—The *concentration of nitric acid above 68—69%, by treatment of dilute* nitric acid with nitrogen peroxide, water, and oxygen, may be effected if the time of treatment is extended, the oxygen used only in slight excess, and the gas velocity reduced. Even so, only 80% nitric acid is produced. A very high concentration results by interaction of the weak nitric acid solution with sufficient excess of liquid nitrogen peroxide, followed by slight agitation with oxygen. When the equilibrium $2NO_2 \rightleftharpoons N_2O_4$ is reached in the treatment of nitrous gases with water, nitric peroxide dissolves, and thereby initiates the interaction $N_2O_4 + H_2O \rightleftharpoons HNO_3 + HNO_2$, the nitrous acid being then decomposed into nitric acid and nitric oxide, and oxidised.
W. J. W.

Red Phosphorus as a Reducing Agent. LUDWIG ROSENSTEIN (*J. Amer. Chem. Soc.*, 1920, **42**, 883—888).—The reactions between red phosphorus and acid solutions of a number of salts have been investigated, and a possible application of this substance as a reagent in qualitative analysis has been indicated. The experiments were effected by boiling the solution with 200 mg. of red phosphorus for a few minutes. Silver salts yield an insoluble phosphide, mercuric and mercurous salts are reduced to the metal, palladium and osmium salts are reduced either to the metal or a phosphide, gold salts are converted into an insoluble phosphide, stannic salts are partly reduced to stannous salts, ferric salts are reduced to ferrous salts, iridic salts to iridous, selenates are reduced to the element or to an insoluble phosphide, molybdates are reduced to quadrivalent molybdenum salts, vanadates are reduced to tervalent vanadium salts, dichromates to chromic salts, and permanganates to manganous salts. Bismuth, lead, cadmium, antimony, and arsenic salts, arsenates and stannous salts, are not reduced by red phosphorus. Tellurates and platinichlorides are reduced very slowly by red phosphorus.
J. F. S.

Carbon Formed in the Reaction between Calcium Carbide and Nitrogen. A. REMELÉ and B. RASSOW (*Zeitsch. angew. Chem.*, 1920, **33**, 139—140).—On decomposing calcium cyanamide

(obtained by the interaction of calcium carbide and nitrogen) with water at 160—180° to produce ammonia, the products of the decomposition included small quantities of carbon. This was freed from the bulk of calcium carbonate by treatment with hydrochloric acid, and was purified by fusion with potassium hydroxide or treatment with hydrofluoric acid. It was thus left as graphitic carbon containing 98·15 to 99·4% C, 0·13 to 1·64% H, and 0·43 to 1·48% of residue. It had $D^{15\cdot5}$ 2·250, ignited at 600—640°, and closely resembled Acheson graphite in its electrical conductivity. When oxidised, it yielded a graphitic acid containing 54·81% C, 1·79% H, and 43·40% O, and showing only very slight colloidal properties. When fused with potassium hydroxide, it reacted (like Acheson graphite) at 500°, with the evolution of hydrogen, whereas Ceylon graphite yielded scarcely any gas at 750°. It was not attacked by strong nitric acid. C. A. M.

Charcoal before the War. II. WILDER D. BANCROFT (*J. Physical Chem.*, 1920, **24**, 201—224. Compare this vol., ii, 309). —A general discussion on charcoal, in which the removal of inorganic matter, such as calcium carbonate and calcium sulphate, from charcoal which has been used in sugar refining is discussed. The decolorising power of bone-black and methods of preparing synthetic bone-black are considered. J. F. S.

Silicon Hydrides. VIII. Halogen Derivatives of Disilane and their Hydrolysis. ALFRED STOCK and KARL SOMIESKI (*Ber.*, 1920, **53**, [*B*], 759—769. Compare A., 1916, ii, 319; 1918, ii, 110, 111; this vol., ii, 31).—The behaviour of disilane, Si_2H_6, towards halogen acids has been investigated, and is found to resemble closely that of monosilane.

Disilane does not appear to react with hydrogen chloride at the ordinary temperature or at 120°; in the presence of a little sublimed aluminium chloride, however, reaction occurs more or less readily, according to the general scheme

$$Si_2H_6 + xHCl = Si_2H_{6-x}Cl_x + xH,$$

and the course can be followed readily by condensation, by liquid air, of all the components, except hydrogen, and measurement of the volume of the latter. The activity of the aluminium chloride appears to vary considerably with different preparations, and a satisfactory explanation of this behaviour is not at present forthcoming. A mixture of chlorides is invariably produced, the equilibrium lying in favour of the intermediate members of the series. Thus with hydrogen chloride (1 vol.) and disilane (less than 1 vol.), the main product is *dichlorodisilane*, very little *monochlorodisilane* being obtained; with the gases in the volume ratio 2:1, much *trichlorodisilane*, in addition to dichlorodisilane, is produced. Complete chlorination is not, however, effected by a large excess of hydrogen chloride. By reason of the small amount produced, it has not been found possible to isolate monochlorodisilane in the pure state. The final purification of dichlorodisilane could also

not be effected, since it forms a mixture of constant boiling point with trichlorodisilane. The experiments, however, indicate that, as in the case of the carbon compounds, mixtures of isomerides are formed in the halogenation of disilane.

The bromination of disilane has been studied in a precisely analogous manner, and *monobromodisilane*, m. p. $-100°$ to $-101°$, has been isolated in a state of purity. As in the case of the chlorination, the tendency towards the formation of higher derivatives is very pronounced; for instance, in the action of equal volumes of hydrogen bromide and disilane, less than one-third of that portion of the latter which undergoes reaction is converted into the monobromo-derivative.

The hydrolysis of the halogenated disilanes corresponds exactly with that of the similar monosilanes. Thus monobromodisilane readily reacts with water to yield the *substance*, $(Si_2H_5)_2O$, colourless liquid, which can be volatilised without decomposition, and, when dissolved in benzene, instantaneously reduces cold silver nitrate, but not copper sulphate, solution. It reacts slowly but quantitatively with sodium hydroxide solution in accordance with the equation $(Si_2H_5)_2O + 8NaOH + 3H_2O = 4Na_2SiO_3 + 12H_2$. The solid products obtained by the hydrolysis of dibromodisilane and more highly halogenated derivatives closely resemble silico-oxalic acid, $(HO_2Si{\cdot}SiO_2H)_x$. They are only slowly hydrolysed further by water, can be dried in a desiccator without marked decomposition, are blackened by silver nitrate solution, owing to the deposition of metallic silver, evolve hydrogen when treated with alkali hydroxide, and finally yield a residue of silicate, and explode feebly when heated on platinum foil, evolving gas and becoming discoloured. Evidently the Si–Si linking remains intact in them. This bond appears to be more stable towards alkali than would be expected from earlier statements. Thus two stages can be clearly distinguished in the action of alkali on $(Si_2H_4O)_x$, namely, a violent evolution of gas with accompanying solution of the substance, and then a much slower, persistent change, which can speedily be brought to an end by warming the solution. The first phase corresponds with the hydrolytic separation of the hydrogen atoms, $(Si_2H_4O)_x + 3H_2O = (HO_2Si{\cdot}SiO_2H)_x + 4H_2O$, whilst the second is due to the gradual conversion of sodium silico-oxalate into sodium silicate and hydrogen. H. W.

Prolonged Action of Carbonic Acid on Silicates and Quartz. C. MATIGNON and (Mlle) MARCHAL (*Compt. rend.*, 1920, **170**, 1184—1186).—Quartz, wollastonite, dioptase, mica, talc, asbestos, and glass, respectively, in aqueous suspension were submitted to the action of carbon dioxide under 10 atmos. pressure for ten years and three months. At the end of this time, all the silicates and the quartz itself were more or less corroded, and varying amounts of silica had passed into solution. Wollastonite showed the greatest signs of attack and the glass the least.

W. G.

Action of Alcohol on the Sulphates of Sodium. GERALD SNOWDEN BUTLER and HORACE BARRATT DUNNICLIFF (T., 1920, 117, 649—667).

Search for an Alkali Element of Higher Atomic Weight than Cæsium. L. M. DENNIS and R. W. G. WYCKOFF (*J. Amer. Chem. Soc.*, 1920, **42**, 985—990).—The alkalis from 3500 grams of pollucite, which contains more than 30% of cæsium oxide, have been examined to see if they contain the next higher homologue of cæsium. The mineral was decomposed by boiling with hydrochloric acid, and, after dilution, filtered. The filtrate was treated with ammonia and ammonium carbonate, whereby a precipitate, consisting mainly of aluminium hydroxide, was obtained. To guard against possible loss of ekacæsium at this point, the aluminium hydroxide was dissolved in sulphuric acid, and the alums thus formed were recrystallised until the ammonium alum had been eliminated. The residual alums were added to those obtained later and treated as described below.

The filtrate from the aluminium hydroxide was evaporated and the residue converted into chlorides, of which 1250 grams were obtained. These were submitted to a series of fractional crystallisations and precipitations with hydrogen chloride. The most soluble fraction, which, according to the order of the solubilities of the alkali chlorides, would contain ekacæsium chloride, was converted into perchlorates, which were fractionally dissolved until the least soluble fraction had been reduced to 10 grams. The end fractions all showed the presence of cæsium alone, and no fraction indicated the presence of ekacæsium when the arc spectrum was examined. The majority of the chlorides were converted into sulphates and fractionated until only 200 c.c. of the saturated solution remained; this, on examination by the arc spectrum, contained only cæsium. The last fraction of the sulphate crystallisation was converted into the alums, and these fractionated, but in no fraction was there any indication of ekacæsium. [See also Richards and Archibald, A., 1903, ii, 366; Baxter, A., 1915, ii, 97.] J. F. S.

Melting Point of Normal Ammonium Sulphate. CARL CASPAR (*Ber.*, 1920, **53**, [*B*], 821).—When heated in an open tube, normal ammonium sulphate softens at about 310°, melts at 336—339°, and decomposes, with evolution of gas, at 355°; in a closed tube it softens from about 360°, and has m. p. 417—423°. The datum, 140°, recorded in the literature is based on a misapprehension, and refers in reality to ammonium hydrogen sulphate.
H. W.

Solubility of Mono- and Di-ammonium Phosphate. G. H. BUCHANAN and G. B. WINNER (*J. Ind. Eng. Chem.*, 1920, **12**, 448—451).—The solubility (grams in 100 grams of the saturated solution) of monoammonium phosphate between 5° and 90° is $18·0 + 0·455t$; that of diammonium phosphate between 10° and 70° is $36·5 + 0·213t$. W. P. S.

Mixed Colloids of Calcium Fluoride. A. Mazzucchelli and D. Vita (*Gazzetta*, 1920, **50**, i, 232—245. See Paternò and Mazzucchelli, A., 1904, ii, 169).—Colloidal calcium fluoride, prepared by pouring potassium fluoride solution into excess of calcium chloride solution, possesses a negative charge, this observation being in accord with the behaviour noted by Lottermoser with silver salts, which in the colloidal state exhibit the sign of the ion in excess at the moment of their formation (A., 1905, ii, 586). Mixed colloidal solutions containing calcium fluoride and another insoluble salt have been prepared by mixing solutions of suitable salts. Moderately stable mixed colloidal solutions are formed by calcium fluoride with $Ca_3(PO_4)_2$, AgCl, AgBr, AgI, Ag_3PO_4, Ag_2S, CuS, $Fe(OH)_3$, and $Si(OH)_4$, the last of these being thus obtained in the colloidal condition in a solution neutral to methyl-orange. Less stable colloidal solutions, obtainable only under certain conditions, are formed with $CaCO_3$, CaC_2O_4, AgCNS, Ag_2CrO_4, Ag_2MoO_4, ZnS, CdS, MnS, $PbCrO_4$, $PbSO_4$ (very slightly stable), and $BaSO_4$. With As_2S_3, immediate precipitation occurs.

T. H. P.

Slaked Lime and Milk of Lime. Bernhard Kosmann (*Zeitsch. Elektrochem.*, 1920, **26**, 173—181).—Polemical: a long discussion on the processes occurring in the slaking of lime, in which the views of Kohlschütter and Walther (A., 1919, ii, 342) are criticised. The author is of the opinion that the slaking of lime consists in a gradual step-wise combination with water, in which the following substances are produced in order: $Ca(OH)_2$, $HCa(OH)_3$, $H_2Ca(OH)_4$, $H_3Ca(OH)_5$, $H_4Ca(OH)_6$, $H_5Ca(OH)_7$, $H_6Ca(OH)_8$, and $H_7Ca(OH)_9$.

J. F. S.

[**Slaked Lime and Milk of Lime.**] V. Kohlschütter (*Zeitsch. Elektrochem.*, 1920, **26**, 181—182).—An answer to Kosmann (preceding abstract).

J. F. S.

An Unusual Deposit of Aragonite from Sea Water. Roger C. Wells (*J. Washington Acad. Sci.*, 1920, **10**, 249—254).—Small crystals of aragonite were found on the walls of a sealed glass tube which had contained sea-water for several years. The most probable explanation of the formation of the deposit is that alkali had been slowly dissolved from the glass, causing partial conversion of calcium hydrogen carbonate into carbonate. The solubility product $[Ca^{++}][CO_3^{--}]$ for the sea-water under consideration is calculated to be $7{\cdot}2 \times 10^{-10}$ at 25°.

E. H. R.

Reactions between Primary Potassium Phosphate and Increasing Quantities of Calcium Hydrogen Carbonate during Boiling. W. Windisch and W. Dietrich (*Woch. Brau.*, 1920, **37**, 177—180, 187—189).—The precipitates obtained by boiling solutions of primary potassium phosphate with increasing proportions of calcium hydrogen carbonate show increasing percentages of calcium, which range from that corresponding with

secondary to that corresponding with tertiary calcium phosphate. The precipitates appear to entrain soluble alkaline compounds, since the alkalinities of the filtrates (due to formation of secondary potassium phosphate) are lower than the calculated values.

L. E.

A Sulphato-chromate Regarded as an Individual Substance. A. DUFFOUR (*Bull. Soc. franç. Min.*, 1919, **42**, 247; from *Chem. Zentr.*, 1920, i, 726).—The author has vainly endeavoured to repeat the preparation of potassium magnesium sulphato-chromate, $2MgSO_4,K_2CrO_4,9H_2O$, described by Etard (this Journ., 1877, ii, 847). Crystals similar to those obtained by the latter separate from a solution containing magnesium sulphate (2 mols.) and potassium chromate (1 mol.), but these are assigned by the crystallographical properties to the series of isomorphous magnesium double sulphates, which they also resemble chemically in losing two-thirds of their water of crystallisation at 120°. A case of mixed crystals of the general composition

$$n[K_2Mg(SO_4)_2,6H_2O]+(100-n)[K_2Mg(CrO_4)_2,6H_2O]$$

is obviously presented; in the present instance, $n=84{\cdot}5$, whereas with Etard's preparation, the analyses of which were confined to the estimation of CrO_3 and of the loss at 250°, the value of n was 64·5. The loss in weight at 250°, however, exceeds the weight of water, since magnesium chromate begins to decompose, with evolution of oxygen, at this temperature. From a solution of a molar mixture of sulphate and chromate, the former separates first isomorphously mixed with 5·5 mols.% of the latter; after separation of the excess of potassium salts, the first mixed crystals of potassium magnesium sulphato-chromate have $n=72{\cdot}4$. From solutions richer in chromate, for example, from such as contain three times as much double chromate as double sulphate, the double salt immediately separates in triclinic crystals ($+2H_2O$). When, however, the solution is allowed to evaporate at 20°, with careful exclusion of any seed of the triclinic salt, a monoclinic *hexahydrate* may be obtained in small amount, the composition of which approximates to that of the mother liquor. The compound is, however, metastable, and, after a few days, shows efflorescent patches of the triclinic dihydrate, into which it is slowly transformed.

H. W.

Crystalline Structure of Zinc Oxide. W. LAWRENCE BRAGG (*Phil. Mag.*, 1920, [vi], **39**, 647—651).—The crystalline structure of zinc oxide has been determined by measurement of the X-ray spectrum. It is shown that the zinc atoms are arranged on two hexagonal space-lattices, their centres corresponding very closely with those of a set of equal spheres in hexagonal close packing. In the latter case, the axial ratio is $a:c=1:1{\cdot}632$, whilst that for zinc oxide is $a:c=1:1{\cdot}608$. The positions of the zinc atoms are identical with those of the hexagonal close-packed arrangement of spheres, if the latter be supposed to contract in the direction parallel to the hexagonal axis, so as to reduce the ratio c/a from

1·632 to 1·608. The oxygen atoms are probably on two hexagonal space-lattices identical with those on which the zinc atoms are situated, and derived from the latter by a movement of translation parallel to the c axis, which brings every oxygen atom into the centre of four zinc atoms arranged at the corners of what is very nearly a regular tetrahedron. The observed spacings agree well with the calculated values; they are: plane (0001), $c/2 = 2·58$ Å.U.; $(10\bar{1}0)$, $a\sqrt{3}/2 = 2·80$ Å.U.; $(11\bar{2}0)$, $a/2 = 1·61$ Å.U.; $(10\bar{1}1)$, 2·47 Å.U. J. F. S.

Atomic Weight of Lead from a Japanese Radioactive Mineral. THEODORE W. RICHARDS and JITSUSABURO SAMESHIMA (*J. Amer. Chem. Soc.*, 1920, **42**, 928—930).—Lead obtained from a mineral crust found at the bottom of a hot spring in Hokuto, Formosa, Japan, has been used for atomic weight determinations. This mineral, according to Hayakawa and Nakano (A., 1912, ii, 1123), contains also cerium, barium, lanthanum, ionium, polonium, and radium, but no uranium or radio-lead. The metallic lead was converted into the chloride, and the ratio $PbCl_2:2Ag$ determined by Richards's method (A., 1914, ii, 653), when, as the mean of three determinations, the value 207·13 was obtained for the atomic weight. This indicates that the material is mainly ordinary lead, with possibly 5% of an isotope of lower atomic weight. J. F. S.

The Separation of the Rare Earths by Basic Precipitation. I. WILHELM PRANDTL and JOHANNA RAUCHENBERGER (*Ber.*, 1920, **53**, [*B*], 843—853).—In its usual form the basic process for the separation of the rare earths suffers from the drawback that the solubility of the precipitated hydroxides or basic salts in the mother liquor is, in general, very small, and the absolute difference in solubility between the hydroxides of neighbouring earths is minimal; in order, therefore, to avoid local excesses of hydroxyl ions and to achieve a reasonably successful fractionation, it is necessary to work with exceedingly dilute solutions which necessitate lengthy evaporations, etc. An amended process is now proposed which permits the use of solutions of any concentration, it being only necessary to ensure that precipitation is sufficiently slow to be truly selective, and that the most sparingly soluble substance actually separates. This can be effected more advantageously by increasing the solubility of the precipitate in the mother liquor than by simple dilution, whilst at the same time the absolute differences in solubility between the precipitates of neighbouring earths is increased and their precipitation is delayed. Since the reaction between ammonia and the salts of the alkaline earths is reversible, $MCl_3 + 3NH_4{\cdot}OH \rightleftharpoons M(OH)_3 + 3NH_4Cl$, its course is dependent on the concentration of the ammonium salt; increase in the concentration of the latter increases the solubility of the earth hydroxide in the mother liquor within certain limits, and delays its precipitation by ammonia.

The authors have attempted to measure the equilibrium of the reaction under varying conditions in the cases of lanthanum, neodymium, and praseodymium, and have obtained similar, but not identical, results by approaching the subject from the two sides. Since it is found that the precipitate does not consist of the pure hydroxide, but of a strongly basic chloride of varying composition, the pure oxides were treated at the requisite temperature with ammonium chloride solution on the one hand and the basic chlorides so formed were subjected to the action of 1, 2, 3, 4, and $5N$-ammonium chloride solution, whilst, on the other hand, the metallic chlorides were treated with the equivalent quantity of ammonia and so much ammonium chloride as to make 1, 2, 3, 4, and $5N$-solutions of the latter at 15°, 30°, 50°, and 100° in closed vessels until equilibrium was established, after which the amount of ammonia and of earth in the solution were estimated. It is found that the solubility of the basic salts (formed from the oxides) in ammonium chloride solution is always less than that of the basic salts obtained by precipitation with ammonia. In either case, the solubility of the precipitates increases to a maximum with $3N$-ammonium chloride solution, and then diminishes. It is also observed that under otherwise similar conditions, the content of the solution in earthy metal, but not that of ammonia, to a marked extent depends on the amount of the precipitate, which indicates an adsorption of the (partly colloidally) dissolved earthy salt by the precipitate. The curves also show that lanthanum is relatively greatly distinguished from the didymium component by its greater basicity, and that neodymium and praseodymium are very similar in this respect. They also indicate an extremely important influence of temperature on the separation process; the lanthanum curves for 2 and $3N$-ammonium chloride solution are so widely separated from the didymium curves at 50° that a separation should be readily possible, whilst, on the other hand, at a slightly higher temperature, but still under 100°, the curves intersect, so that a separation is then impossible. The praseodymium and neodymium curves generally lie very close together and intersect at definite temperatures. The approximation of the curves at higher temperatures is probably explained by the more complete conversion of the precipitate into the hydroxides, the absolute differences between the solubilities of which are very slight.

Basing their procedure on the experiments just detailed, the authors describe a very successful method for the separation of lanthanum from its mixtures with much didymium. The impure oxide is dissolved to a nearly neutral solution in moderately concentrated hydrochloric acid, an amount of ammonium chloride equal to the weight of the oxide is added, and sufficient water to make the solution 2—$3N$ with respect to ammonium chloride. The solution is heated to 50° in a capacious porcelain dish, and a mixture of equal volumes of $4N$-ammonia and $4N$-ammonium chloride solutions is slowly added with vigorous stirring. As soon as a moderate amount of precipitate has been formed (about 5% of the

original oxide) the operation is interrupted, the precipitate is removed, and a second precipitation is effected in the clear filtrate. The alternate precipitation and filtration are repeated in this manner until the filtrate no longer exhibits absorption lines.

H. W.

The Action of Concentrated Sulphuric Acid on Iron. III. CHARLES E. FAWSITT (*J. Soc. Chem. Ind.*, 1920, **39**, 147—148T. Compare A., 1914, ii, 274).—Experiments on the effect of concentrated sulphuric acid of different strengths on a steel containing C, 0·51%; P, 0·046%; Si, 0·083%; S, 0·058%; and Mn, 0·48%, showed that the velocity of attack increased as the acid was diluted from 97% to 90·9% H_2SO_4; it appeared then to drop suddenly at 89·3%, and below 85% increased rapidly. Shaking has an important effect in increasing the velocity of action. Steel which has been made passive by immersion in nitric acid will sometimes resist the action of concentrated sulphuric acid, but at times the treatment fails to afford protection. In some instances partial immersion of a piece of steel in nitric acid has caused the whole piece to resist the action of sulphuric acid. The addition of nitric acid or a nitrate to the sulphuric acid, however, intensifies its action on steel. The effect of the addition of a number of substances to the sulphuric acid was investigated, including potassium persulphate, sodium sulphate, sodium hyposulphite, and arsenious acid, but none of these had any appreciable protective action.

E. H. R.

The Nickel Plating of Aluminium and its Alloys. LÉON GUILLET and MAXIME GASNIER (*Compt. rend.*, 1920, **170**, 1253—1256).—The surface of the aluminium is first prepared by subjecting it to a sand blast. The sand should be capable of passing through a 0·2 mm. sieve, and be used under a pressure of 1500 grams/$cm.^2$ The nickel deposit should not be thicker than 0·01 mm. If a thicker deposit is required it is preferable to apply first a thin deposit of nickel, then a deposit of copper 0·02 mm. thick, and then a further deposit of nickel. [See, further, *J. Soc. Chem. Ind.*, 1920, 492A.]

W. G.

Revision of the Atomic Weight of Tin. Electrolytic Estimation of Tin in Tin Tetrachloride. GREGORY PAUL BAXTER and HOWARD WARNER STARKWEATHER (*J. Amer. Chem. Soc.*, 1920, **42**, 905—917).—The atomic weight of tin has been determined from estimations of tin in stannic chloride. Stannic chloride prepared from very pure electrolytic tin was subjected to a careful fractional distillation, and portions were decomposed under 0·3*N*-hydrochloric acid, and the solution thus obtained electrolysed, using a mercury cathode which was weighed. The metal obtained from the stannic chloride was shown by means of its spectrum to contain less than 0·001% of lead and copper. Two series of experiments were carried out, the first of which gives a mean of 118·700 for the atomic weight, whilst the second series gives 118·707. The mean value of the atomic weight is therefore 118·703 from sixteen experiments. (Cl = 35·457.)

J. F. S.

Revision of the Atomic Weight of Tin. I. BOHUSLAV BRAUNER and HENRY KREPELKA (*J. Amer. Chem. Soc.*, 1920, **42**, 917--925).—The atomic weight of tin has been determined by the analysis of tin tetrabromide by means of silver, and the ratio $SnBr_4$:4Ag obtained; four experiments were carried out, three of which are in good agreement, and yield a mean value of 118·70 for he atomic weight (Br=79·916). The fourth experiment is dis-arded because of an impurity in the silver nitrate used. Other nethods are investigated, (i) the oxidation of tin with nitric acid; his method is useless because of absorbed products in the meta-tannic acid formed; it yields 118·02, which increases to 118·66 vhen the stannic oxide is fused with potassium hydrogen sulphate. 'he electrolysis of diammonium stannic chloride gives a value 119·03, vhich is too high because of difficulties in the complete reduction f the cathode deposit after heating. The synthesis of stannic romide was found to be unworkable on account of the difficulty in stimating the excess of bromine in the stannic bromide.

J. F. S.

Revision of the Atomic Weight of Tin. II. HENRY KREPELKA (*J. Amer. Chem. Soc.*, 1920, **42**, 925—928. Compare receding abstract).—A further series of atomic-weight determina-ions for tin. The method was a determination of the ratio $SnBr_4$: 4Ag. Greater precautions were taken to exclude mois-ure from the stannic bromide. The mean value of the ratio nBr_4 : 4Ag is found from six experiments to be 1·01586, the xtreme values being 1·01580 and 1·01592. From this the atomic eight 118·699±0·016 is calculated. J. F. S.

A New Series of Complex Compounds: Antimonyoxy-odides. A. C. VOURNAZOS (*Compt. rend.*, 1920, **170**, 1256—1259). -When antimony tri-iodide is decomposed by water to give anti-nony oxyiodide there is an indication of the intermediate forma-on of an unstable complex acid, $H_2(SbOI_3)$. In support of this ew it has been possible to prepare the corresponding mercury id copper salts. When antimony tri-iodide and mercuric cyanide equimolecular proportions are warmed in moist amyl alcohol on water-bath for four to six hours *mercury antimonyoxyiodide*, $g(SbOI_3)$, m. p. 78°, is obtained. This compound is decomposed by ncentrated acids, but can be recrystallised from cold dilute hydro-loric acid. It is decomposed by alkali hydroxides. With copper etate under similar conditions antimony tri-iodide gives *copper timonyoxyiodide*, $Cu(SbOI_3)$.

If mercury cyanide and antimony tri-iodide are heated together dry xylene, *mercury antimonyiodocyanide*, $Hg[SbI_3(CN)_2]$, is tained, which, when treated with moist amyl alcohol, gives the timonyoxyiodide described above. If the heating in xylene is ntinued, a *trimercury antimonyiodocyanide*, $Hg_3[Sb_2I_6(CN)_6]$, is tained. Under similar conditions, cuprous cyanide yields *cuprous timonyiodocyanide*, $Cu_6[Sb_2I_6(CN)_6]$. W. G.

The Mathematical Possibility of Increasing the Yield o of Reducing the Proportion of the Reacting Substances i certain Chemical Reactions. II. ANGEL PEREZ HERNANDI (*Anal. Soc. Quim. Argentina*, 1918, **6**, 306—322).—The author method (this vol., ii, 107) is further illustrated by application t the equation $Sb_2S_3 + 8KNO_3 + 3C_2 = Sb_2 + 3K_2SO_4 + K_2CO_3 + 4CO_2 \cdot CO + 4N_2$. W. R. S.

The Properties of Mixtures of Selenium and Antimon H. PÉLABON (*Ann. Chim.*, 1920, [ix], **13**, 121—153).—A micr scopic examination of mixtures of selenium and antimony fus together shows that, for certain proportions of the constituents, tl liquid mixture may be formed of two phases, the densities of whi are nearly equal, and that the only compound that can be obtain in the pure state by direct fusion of the two elements is tl selenide, Sb_2Se_3. A study of the *E.M.F.* of solution of these allo shows that it increases at first with the time, and finally ten towards a constant value. This value will vary with the relati proportions of antimony and selenium present, and if the *E.M.F.* are plotted against the antimony content there is a sharp inflexi corresponding with the selenide Sb_2Se_3. All alloys richer in an mony than the selenide Sb_2Se_3 give piles sensitive to light, tl *E.M.F.* rising sharply on illumination and then dropping slowl the drop becoming sharp when the source of light is removed. Tl red rays are the most active in promoting this effect.

With a pile in open circuit the *E.M.F.* diminishes gradual with rise in temperature, but in closed circuit the *E.M.F.* increas rapidly as the temperature rises.

Curves are given showing the variations in the resistance a thermoelectric power of mixtures of antimony and selenium wi variations in composition and temperature. W. G.

Bibliography of the Metals of the Platinum Grou Platinum, Palladium, Iridium, Rhodium, Osmiu Ruthenium, 1748–1917. JAS. L. HOWE and H. C. HOLTZ (*U. Geol. Survey, Bull.*, 1919, **694**, 454 pp.).

CHEMICAL ABSTRACTS.

Mineralogical Chemistry.

The Oxidation of the Ingredients of Banded Bitumino Coal. Composition of Coal. FREDERICK VINCENT TIDESWE and RICHARD VERNON WHEELER (T., 1920, **117**, 794—801).

Analysis of a Pyrargyrite. CARLOS CASTRO (*Bol. Min. Mex* 1919, 7, 275—277).—The pyrargyrite analysed came from Uni de Providencia, San Felipe, State of Guanajuato, Mexico. T

crystals were separated from matrix and pulverised, and the sulphide mineral was decomposed by heating in a current of chlorine. The mineral consisted of: pyrargyrite, 98·34; argentite, 1·61; pyrite, 0·37%, of which the pyrargyrite was represented by: S, 17·40; Sb, 22·13; Ag, 58·81%. CHEMICAL ABSTRACTS.

Bäckströmite, an Orthorhombic Modification of $Mn(OH)_2$. G. AMINOFF (*Geol. För. Förh.*, 1919, **41**, 473—491).—Black orthorhombic ($a:b:c = 0·7393:1:0·6918$) crystals, occurring with pyrochroite in the calcite veins at the Långban mines, Sweden, are believed to represent a new modification of manganous hydroxide, to which the name *bäckströmite* is given. In composition, however, they are near to manganite, as shown by the following analyses by R. Mauzelius:

	Mn_2O_3.	MnO.	O.	MgO.	CaO.	PbO.
I	77·80	11·69	—	1·68	0·14	0·04
II	—	—	8·19	2·31 (MgO + CaO)		trace

	Sb_2O_3.	Fe_2O_3.	H_2O (+130°).	H_2O (−130°).	Total.
I	0·07	0·14	5·16	3·24	99·86
II	trace	0·43	8·59	3·54	—

Other determinations gave: O (in excess of MnO), 8·15, 8·67; H_2O (+130°), 9·05, 8·57; H_2O (−130°), 3·27, 3·65%. A partial analysis of the associated, altered pyrochroite gave: O, 8·26; H_2O (+130°), 8·31; H_2O (−130°), 3·94%. The crystals are often encrusted with a regular intergrowth of pyrochroite, the rhombohedral modification of manganous hydroxide; and Röntgenograms on the face (010) are identical with those on the face (111) of pyrochroite. It is therefore concluded that the crystals represent double pseudomorphs, the change being bäckströmite ⟶ pyrochroite ⟶ manganite. Other compounds of the type $R''(OH)_2$ belonging to this isodimorphous series are the rhombohedral $Mg(OH)_2$ (brucite), $Ca(OH)_2$, and $Cd(OH)_2$, and the orthorhombic $Ca(OH)_2$ and $Zn(OH)_2$. L. J. S.

Sphenomanganite from Långban, Sweden. GUST. FLINK (*Geol. För. Förh.*, 1919, **41**, 329—336).—Crystals of manganite, D 4·29, exhibiting a sphenoidal habit, but otherwise identical with ordinary manganite, gave on analysis by Mauzelius:

	Mn_2O_3.	MnO.	O.	Fe_2O_3.	MgO.	BaO.	H_2O.	Total.*
I	—	79·60	8·76	0·35	0·87	—	10·16	100·22
II	81·1	8·1	—	0·7	0·6	1·6	7·3	99·4

* Incl. SiO_2 0·11, Sb_2O_3 0·25, CaO trace, PbO 0·10.

CHEMICAL ABSTRACTS (L. J. S.)

Chubutite and the meaning of its Discovery. E. RIMANN (*Anal. Soc. Quim. Argentina*, 1918, **6**, 323—328).—The author points out that lead oxide is dimorphous, as it crystallises in the tetragonal and rhombic systems (Larsen, *Amer. Min.*, 1917, **2**, 18), whilst the known oxychlorides of lead crystallise as follows:

penfieldite, $PbO,2PbCl_2$, hexagonal; *matlockite*, $2PbO,2PbCl_2$, tetragonal; mendipite, $4PbO,2PbCl_2$, rhombic; pseudomendipite, $6PbO,2PbCl_2$, rhombic; lorettoite, $13PbO,2PbCl_2$, and chubutite, $14PbO,2PbCl_2$, tetragonal. It is suggested that the oxychlorides of lead form a continuous series, and that the dimorphism of lead oxide persists in the mixed crystals, although the dimorphous modifications of one and the same oxychloride have not yet been observed. The determination of the optical constants and the melting points of the oxychlorides should be helpful towards elucidating the question. W. R. S.

Baryto-celestine and the Relation of Anhydrite to Celestine and Barytes. WERNER GRAHMANN (*Jahrb. Min.*, 1920, **1**, 1—23).—To elucidate the isomorphous relationships between anhydrite, celestine, and barytes, the thermal method was applied to determine how the transition point of each substance is affected by admixture with one of the others, whilst density determinations of the mixtures were also made. The transition points of the pure substances are: calcium sulphate, 1193°; strontium sulphate, 1152°; barium sulphate, 1149°. For the experiments, the pure sulphates were ground together in the desired proportions and heated in a platinum crucible to a few degrees above the transition point. The cooling curve was then followed by means of a platinum–platinum-rhodium couple. The condition diagrams for the three binary systems are given. Strontium and barium sulphates are miscible in all proportions in both α- and β-forms, and baryto-celestine is therefore a true isomorphous mixture. Calcinm and strontium sulphates are completely miscible in the α-form above the transition temperature, but in the β-form they are isodimorphous. Addition of strontium sulphate to calcium sulphate first raises the transition temperature up to about 20 mols. % $SrSO_4$; then up to 80 mols. % the transition temperature gradually falls to a minimum at 1010°. The saturated β-mixed crystals co-existing at the eutectic temperature contain 55 to 82 mols. % $SrSO_4$. The density curves indicate that the form of strontium sulphate isomorphous with anhydrite should have a density of 3·55, whilst the second form of calcium sulphate should have a density of 3·29. Barium sulphate and calcium sulphate are likewise isodimorphous, and their miscibility is slight, at most 5 mols. % of calcium sulphate in the barium sulphate crystals. The compositions of naturally occurring minerals are in full agreement with the experimental results, and it is suggested that the name baryto-celestine should be confined to minerals containing between 10 and 90 mols. % of barium or strontium sulphate. E. H. R.

Aluminium Sulphate from Chile. ATILIO A. BADO (*Bol. Minero Soc. Nac. Min.* (*Chile*), 1919, **31**, 196—197).—A white, fibrous mineral, referred to keramohalite, gave:

Al_2O_3.	CaO.	K_2O.	Na_2O.	SO_3.	H_2O.
17·76	0·05	trace	0·39	37·38	44·77

A small part (0·367%) of the sulphuric acid is free. According to *Anal. Soc. Cient. Argentina*, **73**, 351, this analysis corresponds with 54·70% $Al_2(SO_4)_3$, and the formula is $Al_2O(SO_4)_2,12H_2O$. This appears to be identical with the basic sulphate investigated by Marguerite (*Compt. rend.*, 1880, **90**, 1354). The mineral forms rhombohedral crystals, and is readily soluble in water. It undergoes hydrolysis in dilute solution, and is capable of coagulating suspended matters. CHEMICAL ABSTRACTS (L. J. S.).

A New Mineral from Katanga. G. CESÀRO (*Ann. Soc. Géol. Belgique*, 1912, **39**, *Bull.* 241; Annexe to vol. 39, *Publ. relatives au Congo Belge*, 41—48).—Crusts of minute, blue or greenish-blue crystals are found on limestone and sandstone in the Étoile du Congo copper mine. The crystals are orthorhombic, with $a:b:c = 0·9844:1:0·7679$ or $0·9771:1:0·7872$; H $5\frac{1}{2}$, n about 1·7, birefringence about 0·120, 2E 55°, optically negative. Qualitative tests show it to be a copper cobalt phosphate, and from the similarity of the crystallographic and optical properties to those of libethenite, olivenite, etc., the formula is probably

$$(Cu,Co)(OH)PO_4.$$

For this mineral the name *cornetite* has been proposed by H. Buttgenbach (*Les Minéraux et les Roches, Liège*, 1916).

CHEMICAL ABSTRACTS. (L. J. S.)

Amblygonite from Ütö. HELGE BACKLUND (*Geol. Foren. Förh.*, 1918, **40**, 757—775).—The mineral had D 3·065, α 1·5910, β 1·6046, γ 1·6125, 2V about 80°, $\rho > v$. The analysis by Sahlbom gave:

SiO_2.	P_2O_5.	Al_2O_3.	Na_2O.	Li_2O.	F.	H_2O.	Total.
3·50	43·40	33·54	2·71	7·84	11·10	2·18	104·27

CHEMICAL ABSTRACTS.

Meta-torbernite I, its Physical Properties and Relation to Torbernite. A. F. HALLIMOND (*Min. Mag.*, 1920, **19**, 43—47).—"Torbernite" from Gunnislake, Cornwall, suffered no loss in weight over 55% sulphuric acid at the ordinary temperature, but over concentrated acid it slowly lost water, amounting to 10·1% after more than a year. This material is really meta-torbernite I (A., 1916, ii, 258), differing from the torbernite hitherto examined (which has D 3·22; refractive indices, ω 1·592, ϵ 1·582; axial ratio, $a:c = 1:2·97$). This natural meta-torbernite I has D 3·683, 3·700, ω 1·623, ϵ 1·625 (N. L. Bowen, 1919), and $a:c = 1:2·28$. When torbernite, D 3·219, is converted into meta-torbernite I by heating under water for several hours at 100°, the density changes to 3·67, and there is a loss in weight of 7·11%, corresponding with the change from $Cu(UO_2)_2(PO_4)_2,12H_2O$ to $Cu(UO_2)_2(PO_4)_2,8H_2O$. The first formula represents torbernite and the latter meta-torbernite I. A morphotropic relation exists between the crystals of the two substances, and the extra four molecules of water are held in layers that alternate with basal layers having the con-

stitution of meta-torbernite I. From the molecular volumes, it i: calculated that this extra water has a density of 1·2 in the crystal
L. J. S.

Pyrobelonite, a New Lead-Manganese Vanadate fron Långban, Sweden. GUST. FLINK (*Geol. För. Förh.*, 1919, **41** 433—447).—This new mineral forms deep-red crystals wit adamantine to sub-metallic lustre, which are orthorhomb ($a:b:c=0·8040:1:0·6509$) with prismatic or acicular habit. I is brittle, without cleavage; H $3\frac{1}{2}$, D 5·377. Associated mineral are hausmannite, barytes, barysilite, pyrochroite, etc. Analyse by Mauzelius gave (Mn : Pb = 7 : 4):

	V_2O_5.	P_2O_5.	PbO.	FeO.	MnO.	MgO.	CaO.	H_2O.	SiO_2
I..................	19·81	0·05	48·99	0·51	25·03	0·66	0·62	n.d.	0·22
II..................	20·26	—	48·74	0·48	24·99	0·53	0·92	n.d.	0·22

The crystallographic and optical characters show a relation t those of descloizite. CHEMICAL ABSTRACTS (L. J. S.).

Gearksutite at Gingin, Western Australia. EDWARD : SIMPSON (*Min. Mag.*, 1920, **19**, 23—39).—This rare minera previously known only in granite-pegmatite at three localities, ha been found as small nodules embedded in Cretaceous greensand a Gingin, forty miles north of Perth. It is white, earthy, and ver friable. Under the microscope, it shows minute, angular particle which are birefringent and have refractive index about 1·44; D 2·710—2·720. Associated minerals are phosphatic nodule glauconite, kaolinite, halloysite, calcite, limonite, quartz grain and some organic matter; gibbsite [$Al(OH)_3$] is also found in a underlying shale. Analysis I is of the greensand matrix free from any visible gearksutite. II, by H. BOWLEY, of a dark gre phosphatic nodule consisting of fluorapatite (57·7%) with calci (11·4%) and included glauconite, quartz (15%), microcline, an organic matter. III of fossil wood petrified by apatite fro greensand at Dandarragan (fifty miles north of Gingin), where is associated with dufrenite and some vivianite and wavellit IV, *by* H. BOWLEY, *of gearksutite*.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2(
I............	59·79	8·15	10·47	0·33	nil	2·96	2·32	2·8
II	17·83	2·24	2·26	—	—	40·60	1·00	1·1
III............	1·26	trace	1·01	—	0·78	53·88	1·17	—

	Na_2O.	H_2O. —	H_2O. +	CO_2.	P_2O_5.	F.	Organic.	Tota less O for
I............	0·17	5·17	4·73	0·25	1·72	0·77	0·42	99·8
II............	0·66	0·04	2·11	5·02	24·80	2·94	0·48	99·8
III............	—	0·22	0·80	1·31	38·80	3·00	0·18	101·1

	Al.	Ca.	K.	Na.	F.	H_2O. —	H_2O. +	O.	Tota
IV	15·38	22·13	0·06	0·06	41·26	0·12	15·88	[4·88]	100·0

* Incl. TiO_2 0·09. † Incl. Cl 0·01.

‡ Incl. Fe_2O_3, 0·03; K_2O, 0·01, present as glauconite; quartz, 0·19; P_2O_5, tra

Gearksutite is readily soluble in cold dilute acids, and the solution etches glass. It is decomposed by a hot dilute solution of sodium hydroxide. No water is lost below 270°, and less than one-fifth at 300°; at 320° the loss is 14·00%. Heated rapidly to a red heat, it gives off hydrofluoric acid in addition to water. Analysis IV corresponds with 86·5 molecular % of

$$CaF_2,AlF_2\cdot OH,H_2O,$$

with 13·5 molecular % of $CaF_2,AlF(OH)_2,H_2O$. The genesis of the mineral is discussed and equations given. In granite-pegmatite it is of pneumatolytic origin; hydrogen fluoride acting on the felspars of the rock gives, in the first place, normal anhydrous salts (cryolite, etc.), and later, with the cooling of the solution, normal hydrous salts (pachnolite and thomsenolite), and, lastly, basic salts (gearksutite, topaz, etc.). In the sedimentary rock at Gingin, the mineral has evidently been produced by the action of carbonated water on fluorapatite and gibbsite.

L. J. S.

Meteoric Iron from Yenberrie, Northern Territory of Australia. JOHN C. H. MINGAYE (*J. Washington Acad. Sci.*, 1920, 10, 314—316).—A mass weighing about 291 lb. was found in 1918 embedded in sandy soil about twenty miles S.S.E. of Yenberrie. The structure is that of a coarse octahedrite with very thin plates of taenite. Anal. I is of the metallic portion, D 7·304. Duplicate determinations gave Ni + Co 7·46, P 0·195, C 0·065. In 100 grams of the iron 0·00026 gram of platinum was found. Tin and gold could not be detected. II is of a black, brittle material found coating pieces of metal from a dark nodule in the centre of the mass. This consists mainly of sulphide and phosphide. III of small, brown plates and laths, extremely brittle and strongly magnetic. It consists largely of schreibersite with magnetite and carbon.

	Fe.	Ni.	Co.	Cu.	P.	S.	C.
I	92·35	5·98	1·43	0·017	0·161	trace	0·073
II	65·38	6·10	0·37	trace	4·14	13·06	4·94
III	73·22	6·35	0·25	0·02	5·02	nil.	2·51

	Cl.	SiO_2.	Ca.	Mg.	O.	Total.
I	0·003	0·140	—	—	—	100·154
II	0·08	—	0·23	nil	5·70	100·00
III	n.d.	0·28	0·20	0·07	12·08	100·00

L. J. S.

Rhythmic Tubular Rust Formation in Meteoric Iron from Cañon Diablo. K. ENDELL (*Kolloid. Zeitsch.*, 1920, **26**, 215—217).—In specimens of meteoric iron, rust (ferric oxide and hydroxide) is found, which penetrates into the iron mass in the form of a tube which exhibits a rhythmic structure. The formation is held to be due to the setting up of local electric currents when the mass is moist, whereby ferrous hydroxide is first formed; this is oxidised, and the ferric hydroxide is deposited. J. F. S.

Analytical Chemistry.

Theory of Gravimetric Analysis, with Special Reference to Sources of Error. L. Moser (*Zeitsch. anal. Chem.*, 1920, **59**, 1—10).—A discussion on the accuracy of general gravimetric methods. Errors which cannot be eliminated completely are those due to solubility of precipitates, induced precipitation, formation of solid solutions, and adsorption, occlusion, and inclusion. Other sources of error, more under control, are those due to the action of atmospheric oxygen or carbon dioxide on the precipitate, contamination from glass vessels, and decrepitation or partial volatilisation during ignition. The different errors may have a compensating effect. W. P. S.

Yellow Light in Polarimetric Determinations. Luis Guglialmelli (*Anal. Soc. Quim. Argentina*, 1918, **6**, 497—499). —To obviate the drawbacks of the use of sodium chloride, Dupont (A., 1897, ii. 77) proposed a mixture of salt and trisodium phosphate; this is found to work very satisfactorily. For its preparation, 1 gram-molecule of disodium phosphate is dissolved in water and treated with 1 gram-molecule each of sodium hydroxide and chloride. The solution is evaporated to dryness and the residue fused. W. R. S.

Colorimetric Estimations with Solutions containing Two Coloured Substances. K. George Falk and Helen Miller Noyes (*J. Biol. Chem.*, 1920, **42**, 109—130).—The authors have examined with much care the principles underlying the ordinary use of the colorimeter for quantitative work, particularly in such cases as the Bendict method for the estimation of dextrose, where two coloured substances are present. From this study, it is shown that there is grave danger of the introduction of serious errors in such methods unless the standard and the unknown solutions are nearly alike in composition and concentration. J. C. D.

A Photographic Turbidimeter. W. G. Bowers and Jacob Moyer (*J. Biol. Chem.*, 1920, **42**, 191—198).—The apparatus, which is described and illustrated, is fashioned so that a strong light is passed through a definite and comparatively narrow column of the substance in question, and what is not lost falls on one side of an oil spot on paper. On the other side of the spot falls a beam of light of equal initial intensity, in the path of which standardised ground glass disks are inserted until equality of illumination is obtained. J. C. D.

Decomposition (or Removal) of Ammonium Sulphide in Qualitative Analysis. F. Feigl (*Zeitsch. anal. Chem.*, 1920, **59**, 12—15).—When a solution containing ammonium sulphide is warmed with the addition of a slight excess of lead hydroxide and filtered, a clear filtrate is obtained which is free from lead and

sulphur. This method is preferable to the usual procedure for removing excess of ammonium sulphide (acidifying and boiling to expel hydrogen sulphide), since colloidal sulphur is not formed and there is no danger of oxidising a portion of the sulphur, with the formation of sulphuric acid, which would interfere with subsequent tests for alkali earths. W. P. S.

Estimation of Bromine. F. WÜNSCHE (*Arch. expt. Path. Pharm.*, 1919, **84**, 328—339).—In order to estimate bromine in organic matter, the substance is dried with sodium peroxide in a nickel basin, first on a water-bath, then on a free flame, and eventually incinerated. The ash is extracted with distilled water and filtered, and the filtrate neutralised with concentrated sulphuric acid and treated with potassium permanganate and sulphuric acid. The free bromine is carried over by means of a current of air into a vessel containing a known volume of magenta and sulphurous acid. The bromine is then estimated colorimetrically by comparing the violet coloration which is produced with a set of standards. Two mg. of neuronal were estimated in 30 c.c. of blood with an error of 12%. Neuronal, adaline, and bromural were estimated in frog's tissue by this method with an error of about 7%. S. S. Z.

Kendall's Method of Estimating Iodine in Thyroid Preparations. S. B. KUZIRIAN (*Proc. Iowa Acad. Sci.*, 1918, **25**, 495—496).—(1) In destroying organic matter, it is advantageous to use more sodium hydroxide and less potassium nitrate to obviate the formation of large quantities of nitrite, which tend to liberate iodine. (2) Organic substances with high ash content often contain iron or some other interfering element, which ought to be eliminated before trustworthy results can be obtained. Filtration at this point does not altogether eliminate the interfering action of ash. When, however, the sodium hydroxide fusion was taken up with hot water, a few grams of sodium carbonate and some talc added, and the solution brought to boiling and kept boiling for a few minutes, set aside for two hours, and filtered, the filtrate was free from interfering basic elements. (3) In acidifying the above filtrate with 85% syrupy phosphoric acid, the author's experience was well in accord with that of Forbes, Beegle, and others, who found that one or two drops of phosphoric acid in excess was insufficient to assure expulsion of all bromine. Even after the addition of 1·5 to 2 c.c. in excess, the whole of the bromine could be boiled off without causing any loss of iodine. This was shown by taking an aliquot of accurately standardised alcoholic solution of iodoform and estimating iodine according to Kendall's method. No loss of iodine occurred when 2 c.c. of acid were added in excess. (4) In boiling off the bromine, it was made a practice to dilute the filtrate to more than 400 c.c. and boil down to 250 c.c., thus assuring a complete expulsion of bromine. Under these conditions, the author found the method applicable

for tankage, roughage, and other organic substances with a high per cent. of ash. CHEMICAL ABSTRACTS.

Modifications in the Technique of Estimating Oxygen in Blood with Van Slyke's Apparatus. E. P. POULTON (*Proc. Physiol. Soc.*, 1920; *J. Physiol.*, 1920, **53**, lxi. Compare A., 1918, ii, 82).—Modifications have been introduced which avoid certain errors due to the presence of dissolved air in the reagents, and which shorten the estimation. Ten c.c. of dilute ammonia are shaken with some crystals of potassium ferricyanide, a trace of saponin, and four or five drops of octyl alcohol. The mixture is placed in the cup and drawn completely into the apparatus, and sealed with mercury. By reducing the pressure, the dissolved air is withdrawn from the reagent, which is then returned to the cup. The blood pipette has a small ring of fine rubber tubing round the tip. By this means, the pipette, when full of blood, is pressed down beneath the ferricyanide mixture on to the bottom of the cup, and on turning the upper tap of the apparatus, the blood is delivered directly into the burette without admixture with the reagent. On removing the pipette, the last portion of the blood is washed in by the ferricyanide mixture, 2 or 3 c.c. of the latter being allowed to remain behind in the cup. The tap is then sealed with mercury. J. C. D.

Detection of Water in Alcohol and other Organic Solvents. F. HENLE (*Ber.*, 1920, **53**, [*B*], 719—722).—When normal aluminium ethoxide is heated at about 340° until the temperature, as indicated by an immersed thermometer, begins to fall, it yields a heavy, yellow, semi-solid mass, the composition of which corresponds with the formula $Al_2(OEt)_4O$; if the action is continued until the thermometer indicates 330° or less, a brittle, yellow resin is obtained, which has the approximate composition $Al_4(OEt)_6O_3$. Both substances are soluble in xylene and are suitable for the detection of water, the latter compound being the more sensitive. The reagent may be readily prepared in a single operation by treating aluminium turnings with absolute alcohol and a little mercuric chloride, heating the product for several hours on the water-bath until the aluminium ethoxide appears dry, distilling off the alcohol of crystallisation at 210—220°, and finally heating the crude aluminium ethoxide at about 340° for an hour. The product is dissolved in about a litre of dry xylene and the solution filtered through a dry paper. The clear, pale yellowish-brown filtrate can be preserved indefinitely in the absence of moisture and air. The test is carried out by adding a few drops of the xylene solution to a few c.c. of the liquid under investigation; according to the quantity of water present, a voluminous, gelatinous precipitate of aluminium hydroxide is produced immediately or after a few seconds. Distinct evidence is obtained in the various cases, with the percentage of water enclosed in brackets after the name of the solvent: ethyl alcohol (0·05), methyl alcohol (0·1), ethyl ether (0·005), ethyl acetate (0·1), acet-

aldehyde (0·1), acetone (1). The two substances last named may also yield a white turbidity, due to the precipitation of excess of the ethoxide, which, however, may readily be distinguished from aluminium hydroxide, as it readily dissolves in xylene or in an excess of the reagent. H. W.

Oxidation in Relation to the Estimation of Sulphites. H. I. WATERMAN (*Chem. Weekblad*, 1920, **17**, 196—197).—The oxidation of sulphite solutions in air, as measured by the increasing volume of the solution required to reduce a given quantity of iodine, proceeds fairly rapidly in the case of sodium hydrogen sulphite and very rapidly in the case of normal sodium sulphite, the hydroxyl ions present in the latter being probably catalytically active. Addition of sodium hydroxide accelerates the oxidation. Accurate estimations of sulphite were obtained by dissolving the salt in a boiled 5% glycerol solution in a flask filled with carbon dioxide. A measured quantity of this solution is run into excess of acid standard iodine solution, also under carbon dioxide, and the residual iodine titrated with thiosulphate. W. S. M.

An All-glass Nitrogen Apparatus. E. R. ALLEN and B. S. DAVISSON (*Ann. Missouri Bot. Gardens*, 1919, **6**, 45—48).—The apparatus is of the usual Kjeldahl form. The advantages claimed are: the elimination of rubber connexions; efficient scrubbing of entrained alkali from the steam; the use of Pyrex glass, which does not yield an appreciable amount of alkali to steam or to boiling solutions. The rigidity may be lessened by one rubber connexion between the distilling bulb and the Kjeldahl flask if the glass ends are kept close together. The distilling bulb has a capacity of 200 c.c.; steam enters it through a re-curved tube with a perforated end. Thus the bulb acts as a trap for scrubbing the steam. CHEMICAL ABSTRACTS.

1. Modified Kjeldahl Method. 2. Carbazole Test for Nitrites. 3. Colour Test for Tryptophan in Urine. W. A. FEARON (*Dub. J. Med. Sci.*, 1920, [iv], No. 1, 28—32; from *Physiol. Abstr.*, 1920, **5**, 79).—(1) The best proportion of the constituents in the acid mixture for incineration is given. Steam distillation is best, but Cole's method of distilling with alcohol is also good and rapid. Methyl-red is recommended as an indicator. (2) All urines give a colour with sulphuric acid, but the tint varies from orange vermilion to deep violet; a large number of substances might give colours: (*a*) pigments and chromogens from bile and blood, and (*b*) from indole and derivatives from intestinal putrefaction which reach the urine via the blood. The red colour is attributed to indole derivatives reacting with the α-nitro-group. Nitrites give a green colour with carbazole. (3) The usual tests are not adequate to detect tryptophan in urine, because of the presence of other indole compounds. If the urine is treated with an excess of the Hopkins-Cole reagent and a drop of the mixture is added to concentrated sulphuric acid, the tryptophan condensation

product (allied to carbazole) gives a deep green colour with the nitrites of urine. Tryptophan in urine is rare. J. C. D.

Sensitive Reaction for Nitrites. P. H. HERMANS (*Pharm. Weekblad*, 1920, **57**, 462—463).—The following gives a sensitive reaction for nitrite in presence of nitrate. To 2 c.c. of the solution to be tested a few drops of glacial acetic acid are added, and then 2 c.c. of 5% potassium oxalate solution, 1 c.c. of 5% manganous sulphate solution, and a few drops of 3% hydrogen peroxide. A red coloration indicates nitrite. 0·02 Gram of sodium nitrite per litre can be detected in this way. W. S. M.

Detection of Arsenic in Sulphur. HAROLD S. DAVIS and MARY D. DAVIS (*J. Ind. Eng. Chem.*, 1920, **12**, 479—480).—Schaeppi's method of detecting arsenic in sulphur (extraction with warm ammonia and treatment of the solution with silver nitrate to precipitate the dissolved sulphide) is untrustworthy, since sulphur itself dissolves in ammonia, and the resulting ammonium sulphide gives a precipitate of silver sulphide. The best method consists in oxidising the sulphur with bromine and nitric acid, and applying the Gutzeit test to the residue. W. P. S.

Iodometric Estimation of Arsenic Acid. P. FLEURY (*J. Pharm. Chim.*, 1920, [vii], **21**, 385—391).—The reaction $As_2O_5 + 4HI = As_2O_3 + 2I_2 + 2H_2O$ is complete in five minutes when the reacting mixture is heated at 100° and contains 25% of potassium iodide and 3·65% of hydrogen chloride. A quantity of arsenate equivalent to about 50 c.c. of $N/10$-iodine solution is dissolved in 30 c.c. of water, 3 c.c. of hydrochloric acid (D 1·171) are added, and the mixture is heated on a boiling water-bath for five minutes; 25% of potassium iodide is then added, the heating continued for a further five minutes, and, after the mixture has been cooled, the iodine is titrated with $N/10$-thiosulphate solution. Owing to the action of dissolved oxygen on hydriodic acid, the amount of iodine is always larger than that which should correspond with the arsenic acid. An excess of sodium hydrogen carbonate is then added to the mixture and the arsenious acid titrated with $N/10$-iodine solution. W. P. S.

[**Estimation of Arsenic Acid in Presence of Arsenious Acid.**] GEORG JOACHIMOGLU (*Arch. expt. Path. Pharm.*, 1916, **80**, 8—24).—See this vol., i, 510.

Spectroscopic Methods for Estimating Carbon Monoxide in Blood. H. HARTRIDGE (*Proc. Physiol. Soc.*, 1920; *J. Physiol.*, 1920, **53**, lxxvii–lxxviii).—The most satisfactory method was found to be one previously described by the author (A., 1912, ii, 488). J. C. D.

The Estimation of Carbon Dioxide and Fermentable Sugars. ARTHUR SLATOR (*J. Soc. Chem. Ind.*, 1920, **39**, 149—151T).—The estimation of carbon dioxide is carried out as follows. The

carbonate solution is placed in a distillation flask connected through the neck opening to a trap leading to a condenser and receiver containing standard barium hydroxide solution. To the side-arm of the distillation flask is connected by means of pressure tubing a small tube containing dilute sulphuric acid. The pressure tubing is clipped, while the whole apparatus is being exhausted, the clip then removed, and the acid in the small tube is boiled over into the distillation flask. The solution in the latter is then boiled, and the carbon dioxide absorbed by the barium hydroxide is determined by titration. The apparatus has been used for determining the quantity of carbon dioxide produced during the fermentation of sugars. The fermentation was allowed to proceed in a small tube sealed off at a fine capillary. The tube was then connected to the side-arm of the distillation flask by pressure tubing, the apparatus was exhausted, the capillary tube broken, and the carbon dioxide boiled over into the receiver. The method serves to characterise enzymes and yeasts by fermenting with them appropriate sugars. E. H. R.

Analysis of Silicate and Carbonate Rocks. W. F. HILLEBRAND (*U.S. Geol. Survey, Bull.* **700**, 1919, 1—285).—The Bulletin is a general treatise on the analysis of rocks; methods are described for the separation and estimation of the common and rare constituents of the rocks, and only those methods which have been found to be trustworthy are recommended. Attention is directed to the frequent occurrence of boron in rocks, but hitherto the estimation of this element has usually been neglected; Chapin's method (A., 1909, ii, 93) is recommended for the purpose. W. P. S.

The Analysis of Natural Silicates. LOUIS DUPARC (*Bull. Soc. franç. Min.*, 1919, **42**, 138—241; from *Chem. Zentr.*, 1920, ii, 680).—A summary and extension of many scattered communications by the author and his pupils on this subject. The work comprises a critical re-examination, discussion, and frequently modification of practically all the important methods of silicate analysis. H. W.

Practical Methods for the Estimation of Radium. III. α-Ray Method, γ-Ray Method, Miscellaneous. S. C. LIND (*J. Ind. Eng. Chem.*, 1920, **12**, 469—472. Compare A., 1915, ii, 486; 1916, ii, 114).—The α-ray method is simple and sufficiently trustworthy for many purposes, but it cannot take the place of a direct radium estimation in such minerals as carnotite, pitchblende, etc. The errors are due to variation in the amount of the loss of radium emanation by gaseous diffusion from the ore, to variation in the radium–uranium ratio, and to the position of the radioactive material in the individual grains of the ore. The γ-method is a convenient means of measuring radium in quantities above 0·1 mg., but the radium preparation must be confined in a closed vessel for one month before the measurement is made, so that the

γ-radiation will have reached a maximum; if the measurement is made earlier a correction must be made for the unelapsed time. Modifications of the interchangeable electroscope (*loc. cit.*) are described. W. P. S.

The Separation and Gravimetric Estimation of Potassium. S. B. KUZIRIAN (*Proc. Iowa Acad. Sci.*, 1917, **24**, 547—550).—Aniline perchlorate is the best reagent to replace platinic chloride for the separation and gravimetric estimation of potassium. The best results are obtained when the following points are observed: The exact strength of alcohol used must be known, and none used that runs below 99·5%. For every 1·5 c.c. of water used for dissolving the mixed chlorides, 50 c.c. of absolute alcohol should be used. The solution of a weighed amount of aniline perchlorate in 50 c.c. of absolute alcohol is added to the solution of the mixed chlorides drop by drop with constant shaking and set aside for one to two hours before filtering, to avoid occlusion of potassium chloride. The chief objections to the perchlorate method are the time and the slight solubility of potassium perchlorate in 95% alcohol. The use of aniline perchlorate in place of perchloric acid so shortens the process as to render it more advantageous than any other method in use for the separation and estimation of potassium; moreover, it affords the best means for the direct separation and estimation of sodium in the alcoholic filtrate.
CHEMICAL ABSTRACTS.

The Carrying Down of Calcium and Magnesium Hydroxides by Precipitates of Ferric Hydroxide. TOPORESCU (*Compt. rend.*, 1920, **170**, 1251—1253).—A second precipitation with ammonium hydroxide is quite sufficient to remove all calcium hydroxide from a ferric hydroxide precipitate. This may also be effected by washing the first precipitate of ferric hydroxide with a boiling 5% solution of ammonium nitrate. The addition of 2% of ammonium chloride to the solution prior to the precipitation of ferric hydroxide does not prevent it from carrying down some calcium hydroxide. Similarly, it does not prevent the carrying down of magnesium hydroxide, and the latter cannot be removed either by simple reprecipitation of the ferric hydroxide or by washing the precipitate with ammonium nitrate. W. G.

Estimation of Mercury. C. M. BOUTON and L. H. DUSCHAK (*U.S. Bureau of Mines, Techn. Paper.* **227**, 1920, 1—44).—The finely powdered mercury ore is mixed with lime and heated in a tube closed at one end. A layer of coarse sand is first placed in the tube, then the mixture, and finally a layer of lime, and the opening closed with a plug of brass wire gauze. The tube is allowed to project 7 to 12 cm. beyond the furnace, which is heated at about 500°. The effect of the sand filling is to reduce the volume of air expelled, and so prevent loss of mercury. In the presence of much sulphur, cupric oxide is mixed with the lime, whilst organic matter is oxidised by adding a small proportion

of potassium chlorate to the sand. The distilled mercury is dissolved off the tube by hot nitric acid, and oxidised by means of potassium permanganate, the excess of which is removed with hydrogen peroxide, and the solution titrated with standard potassium thiocyanate solution, with ferric sulphate or nitrate (free from haloids) as indicator. The method is also applicable to mercury in solution, the metal being precipitated as sulphide, and the precipitate treated as described. [See, further, *J. Soc. Chem. Ind.*, 1920, 492A.] C. A. M.

Petersen's Method for the Qualitative Separation of Cations of the Third and Fourth Groups. P. DE PAUW (*Chem. Weekblad*, 1920, **17**, 191—192).—Various imperfections in Petersen's scheme (A., 1910, ii, 654) are pointed out and discussed. The following alternative scheme is proposed: To the acid hydrogen sulphide filtrate sodium sulphate solution is added, whereby barium, strontium, and calcium (in part) are removed as sulphates. The filtrate contains the ions $Fe^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$. This is treated with solid sodium carbonate and sodium hydroxide. Ammonia is boiled off, and sodium sulphide added. All metals except aluminium are precipitated as carbonates, hydroxides, or sulphides. Dilute hydrochloric acid removes $Fe^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$, $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$ as chlorides, leaving nickel and cobalt as sulphides. To this solution is added solid sodium carbonate and sodium hypochlorite. Zinc and chromium form zincoxide and chromate respectively, which may be separated by means of barium chloride. The residue contains ferric hydroxide, hydrated manganese dioxide, calcium and magnesium carbonates. This is treated with 5% acetic acid containing a little phosphate. A solution of calcium and magnesium acetates is obtained. The residue is dissolved in sodium peroxide and nitric acid, and the iron and manganese separated in the usual way.

W. S. M.

Different Methods of Estimation of Manganese and their Use in the Examination of Plant Ashes and Similar Products. D. H. WESTER (*Rec. trav. chim.*, 1920, **39**, 414—422).—For the estimation of small amounts of manganese a colorimetric method is necessary, and of the four methods examined only one, namely, that of Marshall (compare A., 1901, ii, 350), in which the manganese is oxidised to permanganate by potassium persulphate, is found to be satisfactory. The presence of small amounts of nitric or sulphuric acid or silver nitrate do not interfere with this method. The amount of persulphate used has no influence. The heating in a water-bath for the oxidation should not exceed thirty minutes. The presence of salts likely to be found in plant ashes does not interfere with the estimation, although it is preferable to remove chlorides by a preliminary evaporation with sulphuric acid. If ferric salts are present to an extent of more than 0·05 gram per 100 c.c., they may make it impossible to carry out the

colorimetric comparison, and thus the method may not always be applicable to the analysis of soils. W. G.

Separation of Chromium and Manganese. M. Herschkowitsch (*Zeitsch. anal. Chem.*, 1920, **59**, 11—12).—The manganese and chromium are oxidised to permanganate and chromate respectively, and their solution is heated on a water-bath for some hours with the addition of ammonium sulphate and an excess of ammonia. The chromate remains unchanged, whilst the whole of the manganese is precipitated; the precipitate is collected, washed with 5% ammonium sulphate solution, then with hot water, ignited, and weighed as Mn_3O_4. W. P. S.

Separation of Tin and Antimony. Estimation of Tin by Cupferron. A. Kling and A. Lassieur (*Compt. rend.*, 1920, **170**, 1112—1114).—The antimony is separated from the tin by precipitation with hydrogen sulphide in the presence of hydrofluoric acid. The antimony sulphide is collected, washed, and redissolved in hydrochloric acid with a little potassium chlorate. The solution is filtered, and the antimony reprecipitated as its sulphide, which is collected, dried at 300° in a current of carbon dioxide, and weighed.

To the filtrate from the first precipitation of the antimony sulphide, boric acid is added, and the liquid boiled with a little hydrogen peroxide. After cooling, a 10% solution of cupferron is added, and the white precipitate which forms is collected, washed with cold water, dried, and calcined, and the tin weighed as stannic oxide. The results obtained by this method are very satisfactory. [See, further, *J. Soc. Chem. Ind.*, 1920, 470a.] W. G.

Estimation of Ethyl Alcohol in Mixtures of Alcohol, Sulphuric Acid, and Water. G. S. Butler and H. B. Dunnicliff (*J. Soc. Chem. Ind.*, 1920. **39**, 146—147t).—The free acid, that is, free sulphuric acid plus acidity due to ethyl hydrogen sulphate, is determined by direct titration with standard alkali. The total acid present, including that which has undergone esterification, is determined by evaporating a weighed quantity of the alcoholic sulphuric acid with excess of standard alkali to a pasty consistence, heating in an air oven for half an hour at 120°, extracting with distilled water, and titrating the excess alkali with standard acid. By a simple calculation, from the two determinations, the acid esterified, and hence the alcohol present as ester, can be found. The free alcohol is determined by distillation, followed by a density determination of the filtrate. E. H. R.

The Action of Hydrocyanic Acid on Dextrose. J. Bougault and J. Perrier (*Compt. rend.*, 1920, **170**, 1395—1397).—The action of potassium cyanide on dextrose may be used as a means of estimating dextrose if an excess of the cyanide is used and the mixture is left for at least two days at 20° as the action is slow.

The residual excess cyanide may then be estimated, or the change in rotation, from $[\alpha]_D +53°$ of the dextrose to $[\alpha]_D +1·87°$ of the glucoheptonates, may be determined.

If an excess of sugar is used with a deficiency of cyanide, the whole of the cyanide is destroyed in about ten hours at 20°, and the mixture is no longer toxic. W. G.

An Improved Method for the Estimation of Sugar in the Urine and Blood. P. J. CAMMIDGE (*Lancet*, 1919, **I**, 939).—Further experience with the volumetric method for the estimation of sugar (A., 1917, ii, 276) has confirmed the accuracy of the results given with quantities above 0·5%, but with percentages below that amount too low a reading may be obtained unless further precautions than those described are taken against oxidation, especially in warm weather. When a urine is expected to contain a low percentage of sugar, under 0·5%, and with all blood and other fluids containing smaller amounts, the water to which the iodine solution is to be added should be thoroughly boiled, to expel dissolved air, and cooled immediately before the estimation is to be made. It is also advisable that the alkaline copper solution for sugar estimations with urine be boiled in a small conical flask, provided with a loose funnel as a stopper, instead of in a beaker as previously described, and that the required amount of urine be run into the boiling fluid from a pipette when the air dissolved in the solution and contained in the flask has been expelled. With blood, etc., the 7·5 c.c. of filtrate and 1 c.c. of modified Benedict solution are added after they have boiled for a few seconds. The water used for diluting the iodine solution and for washing out the flasks, etc., should have been recently boiled and cooled. With these additional precautions the method gives uniformly trustworthy figures, even with the small amount of sugar in normal urine and blood. CHEMICAL ABSTRACTS.

Proximate Analysis of Coniferous Woods. W. H. DORE (*J. Ind. Eng. Chem.*, 1920, **12**, 476—479).—Methods are given for the estimation of loss on drying benzene extract, alcohol extract, cellulose, lignin, soluble pentosans, mannan, and galactan. Preliminary hydrolysis is omitted in the estimation of the cellulose and lignin; soluble pentosans are estimated in the chlorination liquors, and mannan and galactan on separate portions of the original material. Analyses of redwood, yellow pine, and sugar pine show that the sum of the constituents, as found by the above-mentioned methods, is slightly over 100% in every case.
W. P. S.

Colorimetric Estimation of Lactic Acid in Urine. POLONOWSKI (*Compt. rend. Soc. Biol.*, 1920, **73**, 475; from *J. Pharm. Chim.*, 1920, [vii], **21**, 449—450).—The urine is clarified by adding from 1 to 3% of egg-albumin and precipitating this with sodium metaphosphate and dilute sulphuric acid. One c.c. of the clear urine is then treated with 5 c.c. of concentrated sulphuric

acid (added slowly to prevent heating) and 5 drops of a 1% codeine solution (in alcohol), and the yellow coloration obtained is compared with those of standards containing known amounts of lactic acid. The results are trustworthy only when not less than 0·001% or not more than 0·01% of lactic acid is present. W. P. S.

Identification of the Cinnamic Ion by means of the "Oxyferric" Catalyst [a Ferric Salt + Hydrogen Peroxide]. G. Denigès (*Bull. Soc. pharm. Bordeaux*, 1919, **57**, 209—212).—In the case of free cinnamic acid or a cinnamate, as little as 0·02 gram of the acid in 1 litre of solution can be detected by adding 1 drop of ferric chloride solution to 2 c.c. of the solution to be tested, boiling, and adding 1 drop of hydrogen peroxide (6—10 vols. oxygen), when the odour of benzaldehyde is observed after shaking for about ten seconds. The sensitiveness of the reaction is increased by adding 1 drop of 10% sulphuric acid with the ferric chloride solution; this procedure also serves for the identification of a cinnamate. In the case of a cinnamic ester one drop (if liquid) or several particles (if solid) of the sample is boiled for twenty to thirty seconds with 6—8 c.c. of dilute sodium hydroxide solution; the solution while hot is acidified with 10% sulphuric acid, 1 drop of ferric chloride solution is added, the mixture is boiled, treated with 1 drop of hydrogen peroxide solution, and again boiled, whereby the odour of benzaldehyde is produced. This method also serves to detect the presence of cinnamic acid in complex mixtures, such as Peru and Tolu balsams.

Chemical Abstracts.

Estimation of Salicylic Acid in the Blood and its Action on the Heart. C. Friderichsen (*Arch. expt. Path. Pharm.*, 1917, **80**, 235—259).—A micro-method for the estimation of salicylic acid in blood. The blood is absorbed by a small piece of blotting paper (about 250 mg.), and weighed in a torsion balance. The paper is then introduced into a test-tube, to which 10 c.c. of a boiling solution of calcium chloride containing 1·5 c.c. of 25% hydrochloric acid per litre is added. It is allowed to remain in contact with the solution for three hours. The calcium chloride solution is extracted with ether. The ether is just evaporated on a water-bath at 32—33°, and any traces left removed by means of a stream of air. The salicylic acid is dissolved in water and estimated colorimetrically. Employing this method the distribution of salicylic acid in the serum and in the blood corpuscles, as well as the action of various doses on the heart, was studied, the results of which are recorded in the communication. S. S. Z.

Two Procedures for the Estimation of Alkali Nitroprussides. Le Her (*Bull. Soc. pharm. Bordeaux*, 1920, **58**, 12—16).—A solution of 1·0 gram of sodium nitroprusside in 50 c.c. of water is filtered and 59 c.c. (*sic*) of the filtrate are neutralised with sulphuric acid and treated with an excess of a ferric salt. The precipitate of Prussian blue is collected, washed with hot water

(these washings are discarded), then several times with a 20% sodium hydroxide solution, and again with water, the combined filtrates containing sodium ferrocyanide are acidified with sulphuric acid and titrated with $0.1N$-permanganate (1 c.c. = 0·03582 gram of sodium nitroprusside).

In the second method a solution containing not more than 0·40 gram of sodium nitroprusside is treated in a 100 c.c. flask with 30 c.c. of $0.1N$-silver nitrate, water is added to the mark, and, after shaking, the liquid is filtered and the excess of silver nitrate in the filtrate and washings is estimated by Denigès' silver cyanide method. CHEMICAL ABSTRACTS.

Differentiation of Vanillin and Heliotropin. A. LABAT (*Bull. Soc. pharm. Bordeaux*, 1919, **57**, 259—260).—To 2 c.c. of sulphuric acid (D 1·84) are added 0·1 c.c. of an alcoholic solution of vanillin or heliotropin and 0·1 c.c. of an alcoholic solution of gallic acid (20%), and the mixture is boiled on a water-bath for two or three minutes. In the case of vanillin, the liquid will assume a yellowish-brown or brown colour, whereas the liquid containing heliotropin will be coloured blue or emerald-green, depending on the quantity of heliotropin present. This reaction serves to detect heliotropin in quantities as small as 0·00005 mg.

CHEMICAL ABSTRACTS.

The Nitrosoindole Test. J. GROENEWEGE (*Med. Geneesk. Lab., Weltevreden*, 1919, [iii], *A*, 177—193).—The red coloration obtained when a peptone culture of certain bacteria is treated with a drop of mineral acid is due to the presence of nitrate in the peptone, and there is no need to add nitrite before the coloration can be obtained. If the peptone medium is inoculated previously with a denitrifying organism, the nitrate is reduced to nitrite and the latter to ammonia or nitrogen, and the medium no longer yields a nitrosoindole reaction when used for the culture of the organisms mentioned (cholera vibriones, etc.). Conversely, the peptone medium freed from nitrate and nitrite as described may be used for the detection of traces of nitrate; the substance to be tested is added to the medium, which is then inoculated with an organism capable of giving a nitrosoindole reaction. W. P. S.

Analytical Characters of Dimethylaminoantipyrine (Pyramidone). JUAN A. SÁNCHEZ (*Anal. Soc. Quim. Argentina* 1918, **6**, 422—428, 513—521).—Various oxidising agents impart a violet colour to solutions of pyramidone. The action of iodic acid is quantitative, each atom of oxygen acting on one molecule of pyramidone; when a solution of the base is treated with excess of iodic acid, iodine is liberated after a few minutes. By means of this reaction the purity of pyramidone may be determined colorimetrically; 0·5, 1, 1·5, 2, 2·5, and 3 c.c. of a 0·1% solution of standard pyramidone are treated in cylinders with water to 3 c.c. bulk, one drop of concentrated sulphuric acid, and 2 c.c. of 1% iodic acid solution. After five minutes, 5 c.c. of chloroform are added to

each tube, and the liquid well shaken. The sample to be tested is treated in the same manner, and the intensity of the violet colour of the liberated iodine in chloroform in each series of tubes compared.

Antipyrine is without action on iodic acid, but absorbs iodine; an admixture of 20% of antipyrine is sufficient to prevent the liberation of iodine by pyramidone. Distillation of pyramidone with ferric chloride or the theoretical amount of iodic acid yields formaldehyde, derived from the oxidation of a methyl group. To detect pyramidone in presence of large quantities of antipyrine, $N/10$-silver nitrate is recommended. This produces after five minutes in the cold, but quickly on warming, an intense bluish-violet coloration.

Pellizzari's reaction (combination of antipyrine with formaldehyde) can be used for the quantitative separation of antipyrine and pyramidone; 5 c.c. of the aqueous solution of the two bases are left for four days with 5 c.c. of formaldehyde, 2 c.c. of hydrochloric acid, and 2 c.c. of water; the liquid is made ammoniacal, when a precipitate of methylenediantipyrine is obtained. The filtrate is treated with chloroform to extract pyramidone.

To detect small quantities of antipyrine in pyramidone, a little of the powder in a porcelain dish is submitted to the action of nitrous fumes from sodium nitrite and sulphuric acid; the antipyrine crystals will acquire a persistent green colour, whilst pyramidone is coloured violet, although only transiently. To prove the presence of pyramidone in coloured or syrupy liquids, 10 c.c. are made alkaline with ammonia and shaken with chloroform. The separated extract is evaporated to dryness, and the residue dissolved in water and tested with silver nitrate. Pyramidone may be titrated with $N/10$-sulphuric acid in presence of methyl-orange, 0·231 gram of pyramidone requiring 10 c.c. of the acid for neutralisation. W. R. S.

Excretion of Quinine in the Urine. M. NIERENSTEIN (Extract from Observations on Malaria, War Office. 1919, pp. 1—79. Compare A., 1919, i, 236).—The thalleioquinine test can only be regarded as a valuable positive test for quinine, a negative result in no way indicating the absence of the drug. Many other qualitative tests for quinine were investigated, but the only one which is regarded as quite trustworthy is Ramsden and Lipkin's technique for carrying out Herepath's test. Encouraging results were obtained with Robertson's test. In testing for quinine in urine the picric acid test is recommended for clinical use.

The estimation of quinine in urine was studied very completely, and the author obtained the best results with Barratt and York's modification of Giemsa and Schaumann's method. By this method the excretion of quinine was fully studied. J. C. D.

General and Physical Chemistry.

Secondary Spectrum of Hydrogen. MEGH NAD SAHA (*Phil. Mag.*, 1920, [vi], **40**, 159—161).—*A reconsideration of the* calculations of Fabry and Buisson (A., 1912, ii, 613) leads to the conclusion that if the Hα line is emitted by a hydrogen atom, the secondary lines are emitted by the hydrogen molecule. J. R. P.

Structure of the Balmer Series of Hydrogen Lines. T. R. MERTON (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 307—320).—The Hα and Hβ lines have been examined by means of an échelon diffraction grating of thirty-five plates, 15·085 mm. thick, and with a grating step of 0·83 mm. The light was subjected to a preliminary analysis by means of a constant deviation spectroscope before passing into the échelon. It is shown that in tubes containing hydrogen and helium at a few millimetres pressure, the resolution of Hα is complete, whilst Hβ shows no definite structure. On cooling the spectrum tube with liquid air, the Hα line appears as a sharp doublet, perfectly resolved, and Hβ also appears as a definite doublet, but the components are not completely resolved and are hazy in appearance. In the case of the Hα doublet, the separation of the components is 0·1446 *A*, and the intensities of the components are in the ratio 10 : 4·6, whilst for Hβ the separation is 0·093 *A*. The half-width of the components is Hα, 0·028 *A*; Hβ, 0·045 *A*. The author is of the opinion that the observations cannot be explained on the basis of simple doublets, and that it is probable that these lines consist of three or more components, which show great variability in their relative intensities under different conditions. J. F. S.

Spectra and Atomic Numbers of the Elements. J. E. PAULSON (*Astrophys. J.*, 1919, **49**, 276—281).—Rydberg's relation between the frequency-difference of certain spectral lines and the atomic weight, $10^3\nu/P^2$, where ν is the frequency-difference and P the atomic weight, is based on a unit which is not fundamental, and the substitution of atomic number for atomic weight gives a better relation. Takiug Rydberg's atomic numbers (E = 0, H = 1, ? = 2, ? = 3, He = 4, Li = 5, etc.), frequency-differences are calculated on the basis of the two formulæ, $\nu = A \log (N+n) + B$ and $\nu = A \log (P+n) + B$, where N is the atomic number, A and B are constants computed by the method of least squares, and n is a whole number, generally small, which may be positive or negative. For the groups of metals examined, the formula for atomic numbers agrees much better with observed frequencies.

CHEMICAL ABSTRACTS.

Atomic Theory and Low Voltage Arcs in Cæsium Vapour. PAUL D. FOOTE and W. F. MEGGERS (*Phil. Mag.*, 1920, [vi], **40**, 80—97; *J. Opt. Soc. Amer.*, 1920, **4**, 145—147).—The *normal* operation of an arc below ionisation may result in the excitation of a single-line spectrum, a single-series spectrum, or a group spectrum consisting of lines of different series. An explanation is offered of fluorescence in vapours of alkali metals. A mechanism of absorption of radiation is described. The cæsium spectrum was photographed for various accelerating voltages from λ 3878 to λ 9208 with plates stained with dicyanin. No evidence of group or single-series spectra was found. The doublet, $1{\cdot}5s—2p_i$ is alone produced under excitation of 1·5 to 3·9 volts accelerating field. The intensity of these lines gradually increases approximately in proportion to the total number of electrons reaching the anode until the ionisation potential is reached. At this point, a pronounced decrease in intensity occurs, this decrease taking place at the voltage at which the complete line spectrum is produced. This affords a strong argument for Bohr's theory. After a certain voltage, the intensity of any line per unit number of electrons reaching the anode attains a saturation value, in agreement with the quantum hypothesis. Only two types of inelastio impact between electrons and atoms of the alkali metal vapours occur, at the resonance and ionisation potentials respectively, and given by the quantum relation $h\nu = eV$, where $\nu = 1{\cdot}5s—2p_1$ and $\nu = 1{\cdot}5s$.

J. R. P.

Extreme Ultra-violet Spectra of Magnesium and Selenium. J. C. McLENNAN, J. F. T. YOUNG, and H. J. C. IRETON (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 67—72).—The spectrum of magnesium for spark in air and arc in air has been investigated in the region between 2026 and 1850 Å.U., and seven new lines recorded. The spectrum of the magnesium arc in a vacuum has been investigated in the region between 2300 and 1400 Å.U., and seven new lines measured. Several of these agree with lines found by Saunders with the spark in hydrogen, and by Handke with the spark in air. The series $\nu = (1{\cdot}5s) - (m,p)$ has been verified for values of m from 2 to 6, but experiments have failed to detect any further lines of the series $\nu = (1{\cdot}5s) - (m,p_2)$, beyond, possibly, the second member. Thirty lines have been recorded in the selenium arc spectrum between 2300 and 1400 Å.U.

J. R. P.

Metallic Spectra Produced in High Vacua. EDNA CARTER and ARTHUR S. KING (*Astrophys. J.*, 1919, **49**, 224—236).—Spectra of manganese, titanium, iron, magnesium, calcium, and cadmium were produced by vaporising the metals at the focus of a beam of cathode rays and photographing the luminescence in the path of the rays. The metallic vapour in all cases except iron assisted the evacuation by absorbing gas molecules, but iron did not, and in order to vaporise it, it was necessary to make the anticathode

the anode. The lines excited were generally those of the arc and furnace spectra, with the following peculiarities: Certain arc and furnace lines are intensified, whilst others are weakened or absent. The tendency to give enhanced lines, that is, the resemblance to the arc spectrum, is marked in the case of cadmium, present also in the cases of magnesium and calcium, but is very slight for iron, manganese, and titanium. Single-line series show a relatively greater intensity than other series lines. The intensity of the ultra-violet lines is relatively high as compared with the arc and furnace spectra. CHEMICAL ABSTRACTS.

Arc Spectrum of Cobalt According to International Normals. FERDINAND DHEIN (*Zeitsch. Wiss. Photochem.*, 1920, **19**, 289—335).—The arc spectrum of cobalt has been measured by means of a concave grating 6·54 metres radius and 20,000 lines per inch. Granular cobalt was placed in a carbon arc burning with a current of 4—6 amps. at 150 volts, and served as the source of light in all measurements. An iron arc was used for the comparison spectrum. The wave-lengths and intensities of 1,384 lines between λ 7417·38 and λ 2590·606 are recorded in tables and compared with measurements of Krebs (*Diss. Bonn*, 1916). The lines due to impurities, nickel, iron, manganese, calcium, copper, silver, titanium, aluminium, magnesium, and vanadium are recorded in other tables. J. F. S.

Absorption Spectra of Thallium, Aluminium, Lead and Tin, and Arsenic. J. C. MCLENNAN, J. F. T. YOUNG, and H. J. C. IRETON (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 7—13).—In addition to the absorptions of thallium discovered by Guthrie (*Diss. Baltimore*, 1908), further absorptions were obtained as arc reversals. These additional absorptions in the ultra-violet region were confined to the two series, $\nu=(2,p_2)-(m,d')$ for values of $m=6$ to 14 inclusive, and $\nu=(2,p_2)-(m,s)$ for $m=5·5$ to 11·5 inclusive. The series $\nu=(2,p_2)-(m,s)$ has been observed for values of $m=10·5$ and $m=11·5$ for the first time. No absorption was obtained in the region 1700 Å.U. with the thallium arc in a vacuum. The absorption spectrum of aluminium consists of fourteen bands in the extreme ultra-violet. As with thallium, these absorptions are given by the series, $\nu=(2,p_2)-(m,d')$ for values of $m=6$ to 14 inclusive, and $\nu=(2,p_2)-(m,s)$ for values of $m=4·5$ to 8·5 inclusive. The series $\nu=(2,p_2)-(m,d')$ has been verified for $m=12$, 13, and 14, and the series $\nu=(2,p_2)-(m,s)$ for $m=6·5$ and 7·5, for the first time. In all, nineteen absorption bands of lead were measured. It is possible that the system of narrow and diffuse absorptions may correspond with the analogous series absorptions of thallium and aluminium. Three absorption bands of tin were obtained, but no identification of series is yet possible. The flame spectrum of arsenic consists of five lines: 3266, 2860, 2760, 2350, and 2288 Å.U., together with four bands with heads at 2634·5, 2570, 2503·5, and 2437·3 Å.U. The arc absorption spectrum con-

sists of four strong unilateral bands, the sharp edges of whic were towards the red, and occurred at wave-lengths 2634·5, 2570· 2503·5, and 2437·31 Å.U. Contrary to expectation, no single-lii absorption or emission was found which could possibly be suppos to correspond with the line 2620 A.U. predicted by Foote ar others. J. R. P.

The Absorption Spectra of the Cobalt Dithiocarbamat and Xanthates. MARCEL DELÉPINE and LOUIS COMPIN (*Bull. Sc chim.*, 1920, [iv], **27**, 474—477).—A comparative study of t absorption spectra of certain of the cobalt xanthates and dith carbamates previously described (this vol., i, 522, 536) shows th from the point of view of absorption, the group $\cdot CS\cdot S]_3Co$ dominat all the singularities of the rest of the molecule. W. G.

Absorption of Light by Methæmoglobin in Neutr Solution and in Solution made Alkaline by Sodiu Carbonate. PAUL HÁRI (*Biochem. Zeitsch.*, 1920, **10** 271—292).—There is a marked difference in the spectroscop behaviour of methæmoglobin in neutral solution and in soluti made alkaline by sodium carbonate. It is suggested that alkaline solution, methæmoglobin is reconverted into oxyhæm globin, and is probably also changed into other hæmoglob derivatives. S. S. Z.

Light Absorption and Fluorescence. VI. Atomic ar Molecular Energy Quanta. VII. Molecular Phase E. C. C. BALY (*Phil. Mag.*, 1920, [vi], **40**, 1—14, 15—31. S A., 1915, ii, 605; 1916, ii, 240).—VI. From the conception of t elementary energy quantum required to shift one electron fr one stationary orbit to another, and the simple assumption th the combining atoms share equally in the energy loss on combi ation and in the future energy changes of the resulting molecu the author arrives at the conception of molecular quanta and mo cular frequency, the latter being the least common multiple of t atomic frequencies. The smallest possible equal amounts of ener which two or more atoms can evolve when combining together a equal to one quantum measured at the frequency which is the lea common multiple of their atomic frequencies. The molecule m also exhibit those frequencies which are characteristic of its co ponent atoms. These conceptions are applied to the elucidati of the observed relationships between the absorption frequenc of compounds.

VII. Chemical reactivity of atoms is due to the attracti exerted by their electromagnetic fields. As a result of this attr tion, an additive complex is formed as a first stage in the reactic The second stage is the joint loss by all the atoms of equal amou of energy, and the formation of a freshly synthesised molec with its infra-red fundamental. The reactivity of molecules is function of their force fields, and the first stage of any reacti between two or more molecules is the formation of an addit

complex, due to the attraction of their force fields. The reactivity of a molecule will depend on the molecular phase in which it exists; the greater the condensation which has occurred in the force field, the less will be the reactivity. J. R. P.

The Photochemical Equivalent Law from the Point of View of the Bohr-Einstein Conception of Light Absorption. O. STERN and M. VOLMER (*Zeitsch. wiss. Photochem.*, 1920, **19**, 275—287).—A theoretical paper in which the discrepancy between the Einstein equivalent law $n = E/h\nu$ is explained by means of Bohr's conception of light absorption. J. F. S.

Mathematical Theory of Photochemical Kinetics. J. PLOTNIKOV (*Zeitsch. wiss. Photochem.*, 1920, **19**, 225—274, 335—348).—A mathematical paper in which, after a general introduction to photochemical kinetics, the author develops the kinetic relationships of irreversible photochemical reactions for the normal case where there is a moderate absorption of light, and also for the limiting cases where there is, respectively, a very strong and a very weak absorption of light. The special cases of polychromatic light, mirror action, and also reactions with circulating reagents and those occurring in cylindrical vessels, are considered, and mathematical relationships developed for them. Reactions which occur in laminæ are dealt with, and the conditions are established for filter action, both internal and external. The author also considers photo-reactions which are accompanied by non-photochemical reactions, and reactions of one photo-active component for the conditions (*a*) where there are two separated photo-active absorption bands, and (*b*) where there are two partly superposed photo-active absorption bands. The case of two active components is considered (*a*) where one component is photo-active and the other is not, and (*b*) where both components are photo-active. The influence of temperature and the order of photochemical reactions are treated, and, finally, the special case is discussed where an inactive component constitutes a light filter. J. F. S.

The Action of Phosphorus, during Oxidation, on the Photographic Plate and its Ionising Power. W. P. JORISSEN (*Rec. trav. chim.*, 1920, **39**, 429—434).—A reply to Centnerszwer and Petrikaln (compare A., 1912, ii, 709). W. G.

The Cleavage of Lactic Acid by Rays of Short Wave-lengths. OSKAR BAUDISCH (*Biochem. Zeitsch.*, 1920, **103**, 59—63).—The author could not confirm Euler's observation that, on exposing lactic acid to the light of a quartz mercury vapour lamp, alcohol is formed (A., 1911, ii, 452; 1912, ii, 407), nor could he confirm the formation of methane by this exposure, as was alleged by Schanz (*Arch. ges. Physiol.*, 1918, **71**, 650). Acetone, according to the author, does not form methane and acetic acid by being exposed in dilute aqueous solution to sunlight for a short time. These products are formed after an exposure of several months. S. S. Z.

Action of Radiations of Different Wave-lengths on Chlorophyll. RENÉ WURMSER (*Compt. rend.*, 1920, **170**, 1610—1612).—In the action of light on chlorophyll in acetone solution in the red, green, and violet portions of the spectrum, it is shown that the photochemical susceptibility varies with the wave-length in a manner proportional to the constant of absorption, except in the neighbourhood of the minimum of absorption, where it decreases more rapidly. The radiations, the frequencies of which correspond with the two principal bands, red and violet, of the chlorophyll, are, for equal absorbed energy, equally active.

W. G.

The Absorption of *X*-rays. R. A. HOUSTON (*Proc. Roy. Soc. Edin.*, 1920, **40**, 34—42).—An expression used to denote the variation of the coefficient of absorption through an absorption band in optics is applied to the absorption bands of the *J*-, *K*- and *L*-homogeneous *X*-radiation, and it is shown that from it can be deduced the number of electrons per atom taking part in the production of the radiation. The seven results given for *K*-rays do not differ greatly from unity, which is the same result as was deduced similarly by the author for the absorption bands of aniline colouring matters and inorganic salts (*Proc. Roy. Soc.* 1909, [*A*], **82**, 606). The mean value by one method of calcula tion is 0·972, and by another 1·01. For the *L*-bands of platinum and gold, the bands appear to be double with either one or two electrons concerned per component, that is, 2 or 4 in all. But for the *J*-bands the result (0·002 for aluminium) suggests that a singly charged hydrogen atom or doubly charged helium atom rather than an electron is the operative cause. The results furnish an independent confirmation of the wave-length of the *X*-rays, and tell against Bohr's model. F. S.

The Law of Mass-Absorption of the Röntgen Rays F. BUTAVAND (*Ann. Physique*, 1920, [ix], **13**, 161—168).—An empirical and approximate relation is shown to hold between the mass-absorption coefficient λ/ρ, where λ is the absorption coefficient and ρ the density, and the atomic weights P_E of the emitting element and P_A of the absorbing element, which, deduced step by step for each series of rays, takes the general form

$$(\lambda/\rho)_n^{1.5} \times P_E/P_A^{1.2} = 13 + 2^{2(n-1)};$$

n refers to the type of radiation, and has for the four series *H*, *J*, *K*, *L* the values 1, 2, 3, 4 respectively.

In the table, the first column refers to the type of radiation, the second to the value of n, the third to the experimental value of the above expression on the left-hand side of the above equation, and the fourth to that calculated from the right-hand expression.

H	$n=1$	14	14
J	2	17	17·5
K	3	29	26
L	4	77	77

A graphical representation of these results leads to the suggestion that there exist two series to be discovered, designated *G* and *M*, the first very "hard" with the value in the last column corresponding with 13·25, and the second very "soft" with the value 270. F. S.

The Measurement of Radium Emanation in Spring Waters. H. GREINACHER (*Physikal. Zeitsch.*, 1920, **21**, 270—272).—A method is described of carrying out the measurements of radium emanation in spring waters by means of small vessels, of 2 litres capacity or less, in place of the large 10- or 15-litre vessels usually employed. The volume of water, V_2, put into a can of volume V is arranged to be equal to $V/(1+\sqrt{a})$, where a is the absorption coefficient of the emanation in water. After shaking, the water is run out and fresh air admitted to take its place. The emanation in the vessel is then measured. Particulars are given for the reduction of the results to Mache units. F. S.

New Determination of the Absolute Value of the Radium : Uranium Ratio. S. C. LIND and L. D. ROBERTS (*J. Amer. Chem. Soc.*, 1920, **42**, 1170—1177).—A standard radium solution was prepared by dissolving 0·2067 gram of 100% radium chloride containing 157·3 mg. of radium in 1 litre of 5% redistilled hydrochloric acid. The radium content of the specimen was controlled by the γ-ray method by comparison with the International radium standard. The clear solution was diluted with 5% hydrochloric acid until 1 litre contained $1{\cdot}573 \times 10^{-6}$ gram of radium, protected by one million times as much barium chloride. This standard solution was used to standardise three electroscope chambers, each of which had two interchangeable leaf chambers. The standardisation was effected by the Bureau of Mines method (emanation method). The same electroscopes were also standardised by the U.S. Bureau of Mines pitchblende standard. The results give as a final average of eighteen determinations, $3{\cdot}40 \times 10^{-7} \pm 0{\cdot}03$ for the ratio radium : uranium. The result agrees with the results of Becker and Jannasch, $3{\cdot}399 \times 10^{-7}$ (*Jahrb. Radioaktiv. Elektronik.*, 1915, **12**, 1—34), and Rutherford and Boltwood, $3{\cdot}4 \times 10^{-7}$ (A., 1905, ii, 568; 1906, ii, 593; 1908, ii, 454; 1914, ii, 788). J. F. S.

The Determination of the Radioactivity of Spring Waters. OTTOMAR NÜRNBERGER (*Physikal. Zeitsch.*, 1920, **21**, 241—245).—Investigations were made on the radioactivity of a group of springs near Brambach, Saxony, by a variety of the special apparatus designed for this work. It was found that the rate of increase of the activity with time for the emanation was different for each spring and characteristic of it, and departed from that obtained for a solution of pure emanation. These differences are attributed to salts and gases dissolved in the natural spring water. F. S.

The Separation of Isotopes. ALEXANDER FLECK (*Natur* 1920, **104**, 565).—It is suggested, as a method of testing furth the chemical separability of isotopes, that an ester, such as eth acetate, should be saponified with baryta containing radium and i isotope, mesothorium-1, and the ratio of the two isotopes estimate in the salt formed during the progress of the reaction. If the rat is unchanged through the reaction, it will indicate that the reactive powers or strengths as bases are the same. F. S.

Nomenclature Questions concerning Isotopes. F. SEKEI (*Jahrb. Radioaktiv. Elektronik.*, 1920, **16**, 411—415).—A di cussion of such terms as Misch elemente, element typus, and Bleia in use in Germany in connexion with isotopes. F. S.

Ionisation and Resonance Potentials of Nitroge Oxygen, and Hydrogen. F. L. MOHLER and PAUL D. FOO (*J. Opt. Soc. Amer.*, 1920, **4**, 49—54).—The ionisation and reso ance potentials have been measured for hydrogen, oxygen, ar nitrogen by the methods previously used for the measurement the critical potential of electron currents in metallic and no metallic vapours (A., 1918, ii, 94, 287; 1919, ii, 42). In the ca of nitrogen, by three methods, the resonance potential is foun to be 8·18±0·10 volts, and the ionisation potential 16·9±0·5 volt The resonance potential corresponds with the nitrogen doublet $\lambda=1492·8$ Å and $\lambda=1494·8$ Å, whilst the ionisation potential corr sponds with the first term of the series converging at $\lambda=730$ The resonance potential, 7·91±0·1 volts, was obtained for oxyge and the ionisation potential has the value 15·5±0·5 volts. The values indicate that $\lambda=1570$ Å is the single-line spectrum of oxyge and the first member of a series converging at $\lambda=800$ Å. Hydroge has a resonance potential at 10·4 volts, the first ionisation potenti is 13·3 volts, and the second 16·5 volts. The first ionisatio potential is for the atom and the second for the molecule, th difference should give the heat of dissociation per gram-molecu of hydrogen. This value is 74,000 cal., whereas Langmuir calc lates the value 90,000 cal., and the value derived from Bohr theory is 65,000 cal. The first ionisation potential is difficult t measure, and if the value be taken as 13·5, the value 65,000 ca would then follow. There is evidence of a slight resonance collisio between 2·5 and 3·5 volts, but the value has not yet been accuratel fixed. J. F. S.

Extrapolation of Conductivity Data to Zero Con centration. II. EDWARD W. WASHBURN (*J. Amer. Chem. Soc* 1920, **42**, 1077—1087. Compare A., 1918, ii, 55).—The author method of obtaining the value of Λ_∞ has been criticised b Kendall (A., 1918, ii, 182) and Kraus (this vol., ii, 217). In th present paper, the author discusses the points which have bee criticised. In answer to Kendall's claim for priority, it is show that the method used by Kendall is only possible when the electr lyte obeys the law of mass action, whilst the method unde

discussion is possible, irrespective of whether the electrolyte obeys the law of mass action or not. In answer to Kraus, it is shown that the assumptions in the two cases are diametrically opposed. Mathematically expressed, Washburn writes

$$\lim_{c=0} 1/K_E \,.\, dK_E/dC = 0,$$

whilst Kraus writes $\lim_{c=0} 1/K_E \,.\, dK_E/dC = -\infty$. J. F. S.

Extrapolation of Conductivity Data to Zero Concentration. CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1920, **42**, 1087—1090. Compare preceding abstract).—An answer to Washburn's paper (*loc. cit.*), in which it is shown that Washburn's results are a necessary consequence of the assumptions made. It is further shown that, whilst Washburn's method may be applicable to any form of curve and at any concentration, the value of Λ_0 will be different for the different concentrations and for the different forms of curve, save in the exceptional case that Λ is a linear function of the concentration, in which case the law of mass action is actually obeyed. J. F. S.

Extrapolation of Conductivity Data to Zero Concentration. EDWARD W. WASHBURN (*J. Amer. Chem. Soc.*, 1920, **42**, 1090—1091. Compare preceding abstracts).—An answer to Kraus, in which the author states that Kraus's criticism indicates that his method of extrapolation has been misunderstood. He therefore applies it to measurements of Wieland, and draws curves to show that, without using any assumption or smoothed curve, the value of Λ_0 for potassium chloride lies at 129·65. J. F. S.

Theory of Electrolytic Ions. XVI. Electrical Conductivity of the Arsinic Acids. RICHARD LORENZ and ERIKA SCHMIDT (*Zeitsch. anorg. Chem.*, 1920, **111**, 175—192. Compare this vol., ii, 482).—The electrical conductivity of arsanilic, *o*-aminotolylarsinic, diaminophenylarsinic, *m*-dihydroxyphenylarsinic, 3-nitro-4-aminophenylarsinic, dichlorophenylarsinic, 3-nitro-4-hydroxyphenylarsinic, *m*-nitrophenylarsinic, and phenylene-1:4-diarsinic acids have been determined at dilutions 1/64—1/1028, and the conductivity at infinite dilution has been extrapolated in each case. The conductivities of the following acids at infinite dilution have been obtained: arsanilic, 370.0; *o*-aminotolylarsinic, 369·0; diaminophenylarsinic, 369·0; *m*-dihydroxyphenylarsinic, 371·0; 3-nitro-4-aminophenylarsinic, 369; dichlorophenylarsinic, 371·0; 3-nitro-4-hydroxyphenylarsinic, 370·0; phenylene-1:4-diarsinic, 369·0; *m*-dinitrophenylarsinic, 369·0. J. F. S.

Measurement of Dielectric Constants using High Frequencies with a Wheatstone's Bridge. HANS JOACHIM (*Ann. Physik*, 1919, [iv], **60**, 570—596).—The measurement of dielectric constants by means of a modified Hertwig apparatus is described (*ibid.*, 1913, **42**, 1099). It is shown that by the introduction of an ionic tube generator, it is possible to carry out the measurements with undamped waves of constant amplitude. The

apparatus is silent and very simple. In the same way, it is possible to use the Nernst method for measurements with rapid oscillations. A number of measurements with various substances are given as a test of the suitability of the method. The dielectric constant of potassium chloride (2·06), potassium alum (2·970), lead chloride (4·29), lead sulphate (3·72), lead formate (2·35), amorphous sulphur (2·84), mercuric chloride (2·58), mercuric cyanide (2·41), and ammonium sulphate (2·56) in the powdered condition has been determined; the values in these cases are indicated in brackets. The temperature-coefficient has been determined down to $-180°$ for several of the substances. The theory of the dependence of the dielectric constant on temperature, the rôle of the dielectric constant in electrolytic dissociation, the dependence of the dielectric constant on the wave-length, and its relation to the structure of the dielectric, are discussed. J. F. S.

The Electrostatic Potential of the Fluorspar Lattice. ELISABETH BORMANN (*Zeitsch. Physik*, 1920, **1**, 55—56).—An error in the calculation of the electrostatic potential of the fluorspar lattice, as given by A. Lande, has led to errors in later calculations of other authors in which this value was used. Thus the compressibility and the heat of formation of the crystal from the ions have been given erroneous values. These are corrected.

CHEMICAL ABSTRACTS.

Activity-coefficient of Normal Potassium Chloride Solution and the Potential of the Normal Calomel Electrode. JAMES A. BEATTIE (*J. Amer. Chem. Soc.*, 1920, **42**, 1128—1131).—The *E.M.F.* of the cell $Ag,AgCl|KCl,N|KHg_x|KCl\,0{\cdot}1N|AgCl,Ag$ has been measured at 25°, and the value $-0{\cdot}10655$ (mean) obtained. Using this value, the activity ratio of *N*-potassium chloride to *N*/10-potassium chloride is found to be 0·7956. Using this value, the potential of the normal calomel electrode is $E = -0{\cdot}2700 + 0{\cdot}5915 \log 0{\cdot}592 \times 1{\cdot}0328 = -0{\cdot}2826$ volt, a value which is in agreement with that of Lewis, Sebastian, and Brighton (A., 1918, ii, 25). The transport number of potassium in potassium chloride does not change much with dilution; the following values are obtained from the present work and that of MacInnes and Parker (A., 1915, ii, 510): (1·0*N*—0·1*N*), 0·496; (0·5*N*—0·05*N*), 0·498; (0·1*N*—0·01*N*), 0·496; and (0·05*N*—0·005*N*), 0·494. J. F. S.

Electrical Conductivity of Pure Salts in the Solid and Fused States. Determination of the Activity-coefficients of Ions in Solid Salts. JNANENDRA CHANDRA GHOSH (T., 1920, **117**, 823—830).

Free Energy of Dilution and the Transport Numbers of Lithium Chloride Solutions. DUNCAN A. MACINNES and JAMES A. BEATTIE (*J. Amer. Chem. Soc.*, 1920, **42**, 1117—1128). —The *E.M.F.* of cells of the type $Ag,AgCl|LiCl(c_1)|Li(Hg)_x|LiCl(c_2)|AgCl,Ag$, without a liquid junction, has been measured

at 25° for cells in which c_1 and c_2 varied between 3·0*N* and 0·001*N*, and a further series of *E.M.F.* measurements has been obtained for cells with liquid junctions of the type Ag,AgCl | LiCl(c_1) ‖ LiCl(c_2) | AgCl,Ag. From the measurements, the activities of the ions and the degree of ionisation of lithium chloride have been calculated. The following values of α have been obtained: 0·001*N*, 0·976; 0·003*N*, 0·962; 0·01*N*, 0·932; 0·03*N*, 0·899; 0·1*N*, 0·834; 0·3*N*, 0·759; 1·0*N*, 0·641; and 3·0*N*, 0·458. By combining the two sets of *E.M.F.* values, the transport numbers of the ions have been calculated, and, where possible, the values have been compared with the best values obtained by the Hittorf method. Since these numbers change rapidly with the concentration, a method has been devised by which the numbers can be calculated from the *E.M.F.* values and expressed as a function of the ion activity. In this way, the value of the transport number at any given concentration can be obtained. The following transport numbers of lithium in lithium chloride are obtained: 0·001*N*, 0·359; 0·005*N*, 0·341; 0·01*N*, 0·334; 0·02*N*, 0·327; 0·05*N*, 0·318; 0·10*N*, 0·311; 0·20*N*, 0·304; 0·30*N*, 0·299; 0·50*N*, 0·293; 1·0*N*, 0·286; 2·0*N*, 0·276; and 3·0*N*, 0·268. J. F. S.

Electrochemical Behaviour of the Sulphates of Thallium. G. GRUBE and A. HERMANN (*Zeitsch. Elektrochem.*, 1920, **26**, 291—297. Compare Abegg and Spencer, A., 1905, ii, 369).—The influence of the current density, acidity, and the anode material on the anodic formation of thallic sulphate in sulphuric acid solution has been investigated. It is shown that low current densities and a high acid concentration increase the current yield, and that a specific action of the anode material is active in the formation. The oxidation potential $Tl^{\cdot}/Tl^{\cdot\cdot\cdot}$ in sulphuric acid solution has been re-measured, and the normal potential found to be $\epsilon_h = +1{\cdot}211$ volts. This value is independent of the acidity and the total concentration over a wide range. The difference between the value of Abegg and Spencer (*loc. cit.*), $\epsilon_h = +1{\cdot}156$, and the present value is probably due to the liquid junction potential not being entirely accounted for in the earlier work. The potential obtained indicates that it is not possible to oxidise thallous sulphate to thallic sulphate in acid solution to a measurable extent by means of oxygen, and, for the same reason, thallous sulphate is unusable as a reaction accelerator of the oxygen electrode in an oxygen–hydrogen electrode with sulphuric acid as electrolyte. The potential of completely oxidised thallic sulphate solutions lies above that of the reversible oxygen potential. Consequently, it was possible to show that in such solutions, the potential of which was $\epsilon_h = +1{\cdot}26$ volts, the bubbling through of oxygen converted some of the thallic sulphate into thallous sulphate. This spontaneous reduction was accelerated by light and platinised platinum. J. F. S.

The Critical State of Ethyl Ether. AUDANT (*Compt. rend.*, 1920, **170**, 1573—1575).—Using an optical method for studying

the critical opalescence and the variation of the critical temperature with the density of filling the tubes, the author obtains for ethyl ether the equation $T_c = 190{\cdot}22° + 11D - 10D^2$, where D is the density of filling. With rising temperature, opalescence commences $0{\cdot}5°$ below T_c and finishes $2{\cdot}5°$ above it, the same limits defining opalescence during cooling. The temperature of maximum opalescence is greater than T_c, and is higher the greater is the density of filling. The intensity of opalescence also increases with the density of filling. W. G.

Equation of State. Fred. G. Edwards (*Chem. News*, 1920 **121**, 3).—A theoretical paper in which equations are given for various quantities. It is stated that the molecular heat equation $k = m^x \log T$ may be converted into the equation of state $b(k + a \log \theta) = m^x \log T$, where θ is the number of degrees below the critical temperature, a an infinitesimal coefficient producing the relative values of the intrinsic pressures at the critical and observational temperatures, respectively, and b is a constant making the sum in brackets equal to the intrinsic pressure, the surface tension, or the volume density with any given units. The values of y obtained from $m = 5{\cdot}95/y$ and $m = 4 - (2y/2{\cdot}95)$ will give the specific heats at variable volume, whilst m will be integral at the natural temperature of change of phase and recalescence. The specific density ratio, $D = Am^x \log T$; the coefficient of linear expansion, $d.V/3d.T = 1/3d.1/Am^x.\log T = T/3Am^x$. The atomic volume ratio, $V = 1/m^x \log T$ is a more general form of the equation of Lothar Meyer's curve, $V = A/D$. J. F. S.

Molecular Heat Equation. Fred. G. Edwards (*Chem. News* 1920, **120**, 277—278).—A theoretical paper in which the author discusses the formula $y = f(\log T - \log \theta)$, in which θ is the temperature at which y is one half the constant $5{\cdot}95$. The expression gives the relation between the entropies of different substances (Lewis and Gibson, A., 1918, ii, 29). J. F. S.

Entropy of Gases. Richard C. Tolman (*J. Amer. Chem. Soc.*, 1920, **42**, 1185—1193).—Making use of his theory of similitude (*Physical Rev.*, 1914, **3**, 244; **4**, 145; 1915, **6**, 219; 1916 **8**, 8; 1917, **9**, 237), the author has deduced the expression $S = 3/2R \log_e m + 5/2R \log_e T - R \log_e p + S_0$ as a general equation for giving the entropy of a gas, $S_0 = 3/2R \log_e a$, and is a general constant independent of the gas. For constant temperature (298° abs.) and constant pressure, the equation becomes $S_{298} = 6{\cdot}87 \log m + c$, where $c = 25{\cdot}1$. The entropy of mercury cadmium, zinc, platinum, molybdenum, tungsten, helium, argon hydrogen (H_2), bromine, iodine, and hydrogen (H) has been calculated by the above equation for 25° and 1 atm. pressure, and the values compared with the experimental values of Lewis and Gibson (A., 1918, ii, 29), and it is shown that where wide extrapolation is not necessary there is very good agreement between the calculated and experimental values. The least agreement is found in the

cases of molybdenum and tungsten, where extrapolation has to be made over 1700° and 2100° respectively; on the other hand, it is to be noted that in the case of platinum, where extrapolation extends over 1500°, there is a rather better agreement between the two values than in the case of hydrogen, where no extrapolation is necessary. J. F. S.

Modified Form of Freezing-point Apparatus. O. MAASS (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 97—99).—To prevent supercooling, a crystal of solid solvent is produced in the solution by the following device. A short piece of platinum wire is sealed through the tube at the side so as to be in contact with the solution. This projects outside the tube into a side-arm in the air jacket, the opening of which passes outside the cooling-bath through a side-neck. When supercooling begins, a small copper cylinder cooled in solid carbon dioxide is introduced through the side-arm and brought in contact with the platinum wire for a short time. A crystal forms on the tip of the wire in the solution. When the freezing point is determined a second time, it is possible to limit the supercooling to one-tenth of a degree. J. R. P.

Latent Heats of Vaporisation of Methane and Ethane. JOHN SATTERLY and JOHN PATTERSON (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 123—127).—Two methods were used. In the first, an electrically-heated wire evaporated some of the liquid, and in the second, a piece of copper was lowered into the liquid. In both cases, the evaporated hydrocarbon was collected over water. The heat supplied was calculated from the watts expended in the first case and the heat capacity of the copper in the second. The results (which are approximate) were: methane, 130 cal. per gram; ethane, 260 cal. per gram J. R. P.

Heat of Sublimation and Valence Forces of Carbon Modifications. K. FAJANS (*Zeitsch. Physik*, 1920, **1**, 101—118. Compare this vol., ii, 354).—The heat of combustion of any aliphatic compound may be resolved into the following effects: nx, where x is the effect of breaking up of the union C–H and n is the number of such unions broken; nv, v being the effect of the sub-reaction $H+\frac{1}{4}O_2=\frac{1}{2}H_2O$ and n, as before, the number of such sub-reactions; ny, where y is the heat effect of splitting the union C–C and n as before; and nz, where z is the effect of the reaction $C+O_2=CO_2$, n as before. From a consideration of the heats of combustion, it is shown that the energy needed to break the single bond group C–C in a saturated hydrocarbon is the same as the energy needed to break up the same group in diamond, where all the atoms are the same distance apart and, therefore, held to each other with the same valence power. This energy is shown to have a value equal to one-half the heat of sublimation of diamond. This value of the heat of sublimation is calculated in two ways: (1) by the equation of Grüneisen; (2) from a consideration of the

change of temperature of the electric arc with the pressure, this temperature being the sublimation temperature of carbon. From the data of Lummer, the heat of sublimation is calculated with the aid of the Clapeyron equation. This value is corrected to that of the heat of sublimation of diamond. The value of the quantity y as given above may then be calculated, and the value of z is obtained from the equation $z+2y=C$, where C is the heat of combustion of diamond. The value of v is calculated from yet other considerations, and the quantity x is then obtained from the equation $-nx+nv-ny+nz=K$ = heat of combustion of some aliphatic compound. The values of these heat effects are as follows: $x=-115,000$ cal., $y=-143,000$ cal., $v=74,000$ cal., $z=381,000$ cal. From these values, the heat of combustion of any aliphatic compound, for example, ethane, can be computed, thus: $-(6\times 115,000)+(6\times 74,000)-143,000+(2\times 381,000)=373,000$ cal. The heat effects of splitting the groups C=C and C≡C can also be calculated. All values given are for 20°. It is also pointed out that, in spite of the difference in the arrangement of the atoms in diamond, graphite, and amorphous carbon, the total energy of the interatomic forces is within 1 or 2% of the same value.

CHEMICAL ABSTRACTS.

Heat of Formation of Water. W. A. ROTH (*Zeitsch. Elektrochem.*, 1920, **26**, 288—291).—A theoretical paper in which the various experimental data on the heat of formation of water are critically discussed, and, as a result, modified data are obtained which are used to recalculate the heat of formation. The results obtained are: heat of formation from hydrogen and oxygen at 18° and under constant pressure is 68·38, 15° Cal., and at 0° the heat of formation of ice is 69·96, 15° Cal. The heat of fusion of ice per gram is 79·67, 15° Cal., and the molecular lowering of the freezing point is 1·860°. J. F. S.

Restatement and Correction of the Thermochemical Data on Organic Compounds. I. The Data of P. V. Zubov. W. SWIENTOSLAWSKI (*J. Amer. Chem. Soc.*, 1920, **42**, 1092—1100). —In a previous publication (A., 1918, ii, 32), the author advocated the use of naphthalene with a heat of combustion of 9612, 15° Cal. as a standard for determining the heat capacity of calorimetric bombs. In the present paper, the author has recalculated the whole of the thermochemical data of P. V. Zubov, obtained at Warsaw between 1892 and 1910 (compare A., 1899, i, 589; 190[illegible] ii, 188; 1904, ii, 159, 382; 1907, ii, 230; 1913, ii, 385, 830). The results for forty hydrocarbons, forty-one alcohols, twenty-three ketones, seven esters, nine acids, and six nitrogen compounds are given in tables, which include the heat of combustion of 1 gram of the substance weighed in air, the molecular heat of combustion (p or v const.), the molecular heat of the substance weighed in vacuum, and the heats of combustion of the substances in the gaseous condition at constant pressure. J. F. S.

Heat of Adsorption of Vapours on Charcoal. ARTHUR B. LAMB and A. SPRAGUE COOLIDGE (*J. Amer. Chem. Soc.*, 1920, **42**, 1146—1170).—The heat of adsorption by charcoal of the vapours of carbon tetrachloride, diethyl ether, chloroform, ethyl formate, carbon disulphide, methyl alcohol, ethyl chloride, ethyl bromide, ethyl iodide, benzene, and ethyl alcohol has been determined at 0° over a considerable range. The resulting values are shown to be reproducible and independent of the rate of adsorption of the vapour and of the previous history of the charcoal. The heat of adsorption in all cases can be represented very precisely as a function of the amount adsorbed by the expression $h = mx^n$, where h is the heat of adsorption per normal c.c. of vapour, x the number of c.c. of vapour adsorbed, and m and n constants which are characteristic of the vapour. The constant n is found to be very nearly unity. The heat of adsorption, therefore, decreases but slightly with increasing amount of adsorption. In other words, there is but slight evidence of fatigue in the adsorptive forces. It has been shown that this decrease, represented by $1-n$, is antibat to the boiling points of the liquids; that is, the liquids with relatively high boiling points exhibit a small value for $1-n$, and hence a slight fatigue. This is due to the fact that such liquids have a high latent heat of vaporisation. The constant m also varies relatively little from vapour to vapour. In general, m and n tend to vary in opposite directions. In agreement with this, the actual molecular heats of adsorption of the various liquids measured are not very different, varying between 12·0 cal. for ethyl chloride and 15·5 cal. for carbon tetrachloride. The heats of adsorption of these vapours are very nearly the same on inactive as on active charcoal of the same kind. Vapours containing halogens appear to react with the charcoal when warmed, so as to decrease the heat developed by any subsequent adsorption of gas, without, however, greatly affecting the fatigue effect. The net heats of adsorption, that is, the heats developed above those corresponding with the latent heats of vaporisation, are approximately of the same magnitude as the latent heats of vaporisation, and the net heats of adsorption per c.c. of liquid are very nearly identical for all the liquids studied. The net heats of adsorption are closely proportional to the heats of compression under high pressure. This indicates that the liquids are all attracted by the charcoal with substantially the same force, and that the net heat of adsorption is merely a heat of compression. The absolute value of this attractive force appears to be about 37,000 atmospheres where 1 c.c. of liquid is adsorbed on 10 grams of charcoal. The molecular adsorbability, that is, the number of c.c. of gas adsorbed at a fixed gas pressure (20 mm.), is inversely proportional to the molecular volume of the liquid. The molecular adsorbability is inversely proportional to the net molecular heat of adsorption. This regularity follows from the previously mentioned regularities. All the above evidence indicates that the liquid films studied are at least one, and usually very many molecules thick, and this is

confirmed by a consideration of the actual volume occupied by the liquid and the approximately known capillary volume and surface of the charcoal. J. F. S.

"Vapour Density" a Misnomer. PHILIP BLACKMAN (*Chem. News*, 1920, **120**, 292).—The author maintains that the term vapour density is incorrect for the quantities usually called by this name; these are in reality vapour specific gravities. The term vapour density should be used for the weight of unit volume of a gas or vapour under standard conditions. J. F. S.

Variation of the Coefficient of Viscosity of Gases with Temperature. ROBERT CLARK (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 177—180).—If two vessels of known volumes be connected by a capillary tube, any pressure difference between them will gradually disappear, owing to flow through the capillary. This flow can be calculated in terms of the rate of change of pressure difference and the volumes of the two vessels; from the dimensions of the capillary tube, the coefficient of viscosity may be determined. If the rate of change of pressure be observed when the apparatus is maintained at different temperatures, the values of the coefficient of viscosity corresponding with these temperatures may be obtained. The viscosities of carbon dioxide, hydrogen, and dry air at temperatures between 0° and 110° were determined, and the value of the coefficient n in the equation $\mu=\mu_0(T/273{\cdot}1)^n$ found to be: air, 0·750; carbon dioxide, 0·965; hydrogen, 0·700. The viscosity of air at 23·0° was found to be $184{\cdot}0\times10^{-6}$. J. R. P.

The Effect of the Addition of certain Fatty Acids on the Interfacial Tension between B.P. Paraffin Oil and Mercury. SHANTI SWARUPA BHATNAGAR and WILLIAM EDWARD GARNER (*J. Soc. Chem. Ind.*, 1920, **39**, 185—187T. Compare Wells and Southcombe, *ibid.*, 51T).—The measurements of interfacial tension between the oil and mercury were made by the dropping pipette method, as described by Donnan (A., 1900, ii, 201). The four acids used were oleic, stearic, linolic, and palmitic acids, and curves are given showing the surface tensions of solutions of varying concentrations of these acids in B.P. paraffin oil. The curve for oleic acid shows a point of inflexion at a concentration of about 0·25%. The curves for oleic, stearic, aud palmitic acids are very similar in character, especially at the higher concentrations, but the surface tensions of the linolic acid solutions are much lower than those of the corresponding solutions of the other three acids. The curves obtaiued are very similar to those given by Langmuir for fatty acids (A., 1917, ii, 525), and, applying Langmuir's views, it would appear that the increased efficiency as a lubricant of a mineral oil to which an organic acid is added runs parallel with a lowering of tension at the metal-oil interface. W. G.

Density of Adsorbing Materials. STUART McLEAN (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 197—199).—The density of

materials was found by the volumenometer method, using helium as the filling gas, since it is not adsorbed at ordinary temperature. The following mean results were found: coconut charcoal (heated to 400°), 1·53; lignite carbonised at 350°, 1·33; lignite carbonised at 450°, 1·46; lignite carbonised at 550°, 1·44. J. R. P.

Properties of Wood Charcoal. ALWYN PICKLES (*Chem. News*, 1920, **120**, 301—302).—It is shown that coconut charcoal, prepared by heating at 900°, becomes more efficient towards a gas on keeping for some time in the air; this may be due to sorption of water, but it is also due to a spontaneous disintegration of the charcoal. Prolonged heating increases the efficiency of the charcoal, and treatment with acid removes sulphur as hydrogen sulphide and prevents friability. Birch charcoal is a more efficient absorber of colouring matter than animal charcoal, and since its density (1·46) is about one half that of animal charcoal, mechanical stirring is not required to the same extent. The adsorption of water from solutions of alkali haloids (negative adsorption) has been investigated at various temperatures. It is shown that at 40° the negative adsorption suddenly increases, and it is at this temperature that the interior of the charcoal is becoming opened out by the solvent action of the solution. It is very probable that the first removal of the water from the solution is due to the surface effect of the charcoal (true adsorption) and that as the temperature rises this effect diminishes with the decreasing surface tension of the water. The interior, or absorption, effect, however, continues to increase and speedily more than counterbalances the decreasing surface effect.

The following types of substances are negatively adsorbed from aqueous solutions: (i) those of simple structure; (ii) highly ionised substances; (iii) compounds with a strongly electropositive cation; (iv) compounds with a univalent metallic cation; (v) compounds having ions with a high mobility. J. F. S.

Effect of Pressure on Gas Adsorption. ALWYN PICKLES (*Chem. News*, 1920, **121**, 1—2).—Equal volumes of charcoal (50 c.c.) from birch chips, coconut, fruit-stone dust, palm nut, almond, and birch dust were rendered free from air by heating and saturated with ammonia at ordinary pressure and temperature. They were then placed individually in an air-tight glass vessel fitted with a manometer and an aspirator tube, and the pressure reduced to a measured point. The apparatus was closed and the change of pressure with time observed. The initial pressures were about 20, 40, and 60 cm. In all cases the pressure at first increased, and eventually (one to two hours) decreased, but in no case was the initial pressure regained. The first effect of aspiration is to remove the gas on the charcoal surface, then gas escapes from the interior, and so increases the pressure, the subsequent decrease being due to surface condensation. The results give an indication of the inner structure of the charcoal. Where a rapid increase of pressure occurred, a complex internal structure may be

assumed (coconut and fruit-stone charcoal). In the case of birch dust, the gas-adsorbing capacity is mainly a surface effect. Palm-nut charcoal was used in large pieces, and it retained the gas mainly by absorption. The apparent density, *AD*, and the true density, *D*, have been determined for each variety used, and the following values obtained: almond, *AD* 0·48, *D* 1·70; birch chips, *AD* 0·23, *D* 1·44; fruit stone, *AD* 0·68, *D* 1·72; birch dust, *AD* 0·21, *D* 1·47· coconut, *AD* 0·63, *D* 1·71; and palm nut, *AD* 0·64, *D* 1·59. The carbon content of all varieties was about 85%. The porosity of charcoal dust is increased by mixing it with solid ammonium dichromate and heating out of contact with air. In this way, the gas-absorbing efficiency per c.c. of actual charcoal is increased, but per c.c. of the whole product it is decreased. As gas adsorbents, the denser charcoals are the most efficient; the order of efficiency is palm nut, coconut, fruit stone. J. F. S.

Adsorption of Gases by Carbonised Lignites. STUART McLEAN (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 187—199).—The adsorption of air, carbon dioxide, oxygen, hydrogen, and nitrogen by lignite was studied. Oxygen is adsorbed much more readily than nitrogen. The presence of water vapour decreases the amount of gas adsorbed. No permanent adsorption takes place, since there are but few cases where the last weight is greater than the first, and these may be due to experimental error. Chemical action may be taking place in the case of oxygen. The fact that in most cases the last weight is less than the first indicates that the oxygen combines with the lignite, forming carbon dioxide, which is given off when the lignite is heated, making the sample lighter.

J. R. P.

Velocity of Sorption. ALWYN PICKLES (*Chem. News*, 1920, **121**, 25—27).—The sorption by charcoal of benzoic acid from alcohol solution at 14°, iodine from *N*/10-potassium iodide solution at 15°, 25°, 50°, and 70°, and potassium permanganate in *N*/10-concentration from water at 12°, 25°, 50°, and 70°, has been determined with respect to the velocity with which these substances are taken up. It is shown that, on applying the equation for unimolecular reactions to these cases, a "constant" is obtained which continually decreases, but by using the equations

$$K = 1/t\{\log_e a/(a-x) - 0{\cdot}4343x/a\}$$

and $K = 1/(t_2 - t_1)\{\log_e (a - x_1)/(a - x_2) - 0{\cdot}4343(x_2 - x_1)/a\}$ a very fair constant is obtained in the case of iodine and benzoic acid, whilst very irregular values are obtained for permanganate. These are attributed to catalytic decomposition of the permanganate by the charcoal, solvent action of the solution in opening up the charcoal capillaries, and the reducing effect of the charcoal. In all the above cases birch-dust charcoal was used.

The velocity of sorption of ammonia and hydrogen chloride by coconut charcoal has been determined at 13°. In the case of ammonia, the "constant" of the unimolecular equation falls steadily with time, but the equations mentioned above give a good

onstant. With hydrogen chloride, the "constant" of the nimolecular reaction gives a moderately good constant, but the alue of K increases rapidly with time, which seems to show that he hydrogen chloride is continually opening up fresh surfaces.

J. F. S.

The Absorption of Colouring Matters by Charcoal. DMUND KNECHT (*J. Soc. Dyers and Col.*, 1920, **36**, 201).—Knecht eplies to the statement by Philip, Dunnill, and Workman (T., 920, **117**, 302) that Knecht and Hibbert (*J. Soc. Dyers and Col.*, 916, **32**, 226) correlate the activity of a charcoal in decolorising olution with its nitrogen content, and shows their original contenion to be that whilst for a basic dye, such as methylene-blue, the itrogen content does not affect the absorptive power, for an acid olour, such as crystal-scarlet, the absorptive power of an animal harcoal is in proportion to its fixed nitrogen content. This conention has not yet been controverted. Knecht still regards the bsorption of methylene-blue as being connected with the oxygen ontent of the charcoal. A. J. H.

The Deliquescence and Drying of Ammonium and lkali Nitrates and a Theory of the Absorption of Water apour by Mixed Salts. E. B. R. PRIDEAUX (*J. Soc. Chem. nd.*, 1920, **39**, 182—185T).—The author has measured the vapour ressures of saturated solutions of ammonium nitrate, potassium itrate, and of a solution saturated with ammonium nitrate and odium nitrate. The results of the latter determinations show the dded difficulty of drying an impure salt, and also, if such has to e dried, that raising the temperature is not necessarily and in all ases advantageous. If the ratio, relative humidity of salt to elative humidity of air, is greater than 1, drying is possible, and he speed of drying could probably be expressed by the van't Hoff aximum work expression, $4{\cdot}57T\log p_1/p$ for 18 grams of water, here p_1 is the pressure of water vapour in the atmosphere and is the pressure of water vapour in equilibrium with the uniariant system, salt–saturated solution–vapour, at a given emperature.

The gains in weight of sodium nitrate plus varying amounts of odium chloride in atmospheres of different humidities have been neasured. The manner in which deliquescence occurs in a mixture f soluble salts is discussed, and it is considered that such eliquescence takes place in two stages. W. G.

The Adsorption Capacity of Cellulose. Remarks about he Electrometrical Micro-analysis of Chlorine. P. RONA nd L. MICHAELIS (*Biochem. Zeitsch.*, 1920, **103**, 19—30).—Cellulose does not appreciably adsorb surface-active non-electroytes. Only in the case of extremely surface-active substances can ery slight adsorption be established. The more marked adsorpion of dyes by cellulose is due to the ash content of the cellulose.

The estimation of chlorine by the electrical method with a alomel electrode is described and discussed. S. S. Z.

The Condition of Dissociation of Ampholytes. I. The Influence of Univalent Ions Disregarding all Colloidal Phenomena. L. MICHAELIS (*Biochem. Zeitsch.*, 1920, **103**, 225—243).—A theoretical discussion of the influence of ions on the dissociation of acids, bases, and ampholytes, for which they have a chemical affinity. S. S. Z.

Process of Diffusion Through a Rubber Membrane. H. A. DAYNES (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 286—307).—The diffusion of hydrogen, nitrogen, oxygen, carbon dioxide, nitrous oxide, and ammonia through rubber sheets has been examined by means of the katharometer (this vol., ii, 503). It is shown that the behaviour of a set of rubber films agrees in all respects, within the limit of the experiments, with that predicted from assumptions of a simple process of diffusion through a rubber membrane. The conclusion previously reached, that the surface resistance is negligible, is thus confirmed. The method furnishes a rapid and satisfactory means of measuring the absorption and the diffusion constant of a material for a gas, and is capable of a high degree of precision. The mean value of the diffusion constant for the three films examined was $11\cdot4\times10^{-6}$ cm./sec. at 20°, the actual values being $11\cdot7\times10^{-6}$, $10\cdot4\times10^{-6}$, and $13\cdot6\times10^{-6}$ cm./sec. The mean value of the absorption coefficient was 0·035 at normal pressure and 20°, the actual values being 0·035, 0·037, and 0·031. The coefficient of absorption has a low temperature-coefficient, approximately 0·5%/1°, compared with that of the diffusion constant. It is not that which is responsible for the great variation of permeability with temperature. This suggests that the process of absorption is a simple molecular action. J. F. S.

The Cause of the Influence of Ions on the Rate of Diffusion of Water Through Collodion Membranes. II. JACQUES LOEB (*J. gen. Physiol.*, 1920, **2**, 563—576).—The effect of ions carrying charges of different signs on the free osmosis of water through a collodion membrane which separates it from a solution of an electrolyte has been discussed previously (compare this vol., ii, 94, 233, 234). It is now shown that the influence of the concentration of electrolytes on the rate of transport of water through collodion membranes in electrical endosmosis is similar to that in the case of free osmosis.

On the basis of Helmholtz's theory of electrical double layers, this influence of an electrolyte on the rate of diffusion of water through a collodion membrane is due to the ions increasing or decreasing the density of charge on the membrane. The relative influence of the oppositely charged ions on this density is not the same in all concentrations. The influence of the ion with the same sign of charge increases in the lowest concentrations more rapidly with increasing concentration than the influence of the ion with the opposite sign of charge, whilst for somewhat higher concentrations the reverse is true. W. G.

The Reversal of the Sign of the Charge of Membranes by Hydrogen Ions. JACQUES LOEB (*J. gen. Physiol.*, 1920, **2**, 577—594).—When a collodion membrane is treated with a protein, the membrane assumes a positive charge when the hydrogen-ion concentration of the solution with which it is in contact exceeds a certain limit (compare preceding abstract). By this treatment, a thin film of protein adheres to the membrane, and the positive charge of the membrane is localised in this protein film. The hydrogen-ion concentration at which the reversal in the sign of the charge of a collodion membrane treated with a protein occurs varies in the same sense as the isoelectric point of the protein with which the membrane has been treated, and is always slightly higher than that of the isoelectric point of the protein used. Thus the critical hydrogen-ion concentration required for the reversal appears to be that concentration where enough of the protein lining of the membrane is converted into a protein–acid salt, for example, gelatin nitrate, capable of ionising into a positive protein ion and the anion of the acid used. W. G.

Atomic Structure and Crystal Symmetry. HANS THIRRING (*Physikal. Zeitsch.*, 1920, **21**, 281—288).—A theoretical paper in which the symmetry of crystals, particularly that of the diamond and sylvine, is considered. Since the reflexion of Röntgen rays from the lattice surface of a crystal depends only on the number of electrons per unit surface, and is independent of the orientation of the atoms, account must be taken of the possibility that the length of edge of the elementary cube of the atom lattice is an integral multiple of that of the corresponding point lattice. This multiple is represented by n, and, taking account of this possibility, the following points are deduced: The carbon atom cannot possess a cylindrical symmetry, that is, it has not a Bohr single-plane system of electrons. Systems with crossed electron rings cannot be brought into line with the symmetry of the diamond; on the other hand, those systems to which Landé attributes a tetrahedral symmetry may be brought into line with the diamond symmetry. The explanation given by Bragg ("*X*-Rays and Crystal Structure," p. 158) for the hemihedrism of potassium chloride, namely, that the atoms do not occupy exactly the corners of the cube or the middle points of the surfaces, but positions a little removed from them, must be abandoned, because this explanation leads to the value $n=2$, which does not agree with any equilibrium position. It is not possible to construct a regular enantiomorphic symmetry for potassium chloride from axial symmetric atoms so long as the assumption is maintained that no potassium or chlorine atom is different from the others. Using Landé's atom model, the hemihedrism of potassium chloride can be explained by $n \geq 2$ if it is assumed that the magnetic forces set up by the potassium atom play an important part in the properties of the symmetry of the crystal. From the holohedrism of sodium chloride, it follows that the magnetic forces of the alkali metals decrease down the periodic system group in the sense that

they are *unnoticeable in the case of sodium*, but in the case of potassium they exercise an influence on the crystal symmetry.
J. F. S.

Crystallisation of Supersaturated Solutions and Supercooled Liquids. D. McIntosh (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 265—272).—The sizes of particles of solid which induce crystallisation of supersaturated sodium sulphate solution and supercooled salol were found to be: sodium sulphate, 10^{-13} to 10^{-18} gram in one method, 10^{-12} to 10^{-14} gram in another; salol, 10^{-9} gram to 4×10^{-15} gram. These are much below the numbers formerly accepted. J. R. P.

Periodic Precipitation. I. Silver Chromate in Gelatin. Alexander Mitchell Williams and Mary Russell MacKenzie (T., 1920, **117**, 844—852).

Composition of the Vapour and Liquid Phases of the System Methane–Nitrogen. H. A. McTaggart and E. Edwards (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 57—66).—The temperature–composition diagram for the system methane–nitrogen at atmospheric pressure was obtained, and the constants in the formula $\log r' = a + b \log r$, where r = ratio methane/nitrogen in liquid, and r' the corresponding ratio in the vapour, determined as $a = -0{\cdot}47$, $b = +0{\cdot}85$. J. R. P.

Velocity of Reactions. M. Polanyi (*Zeitsch. Elektrochem.*, 1920, **26**, 228—231).—A theoretical paper in which certain difficulties in the deduction of the equations for the velocities of reactions are discussed (compare Herzfeld, A., 1919, ii, 503; Polanyi, this vol., ii, 238). J. F. S.

Reaction Isochore and Velocity of Reaction from the Statistical Point of View. M. Polanyi (*Zeitsch. Elektrochem.*, 1920, **26**, 231).—A correction of some of the mathematical expressions in a previous paper (this vol., ii, 238). J. F. S.

The Ignition of Gases. I. Ignition by the Impulsive Electrical Discharge. Mixtures of Methane and Air. Richard Vernon Wheeler (T., 1920, **117**, 903—917).

Colloidal Solutions and Organic Syntheses. II. Mechanism of the Synthesis of Nitrobenzylidene Diacetate. M. Bakunin and F. Giordani (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1917, [iii], **23**, 39—50. Compare A., 1916, ii, 421).—The authors have investigated the equilibrium of the reaction,

$$(CH_3{\cdot}CO)_2O + NO_2{\cdot}C_6H_4{\cdot}CHO \leftarrow NO_2{\cdot}C_6H_4{\cdot}CH(OAc)_2,$$

both without solvent and in ethereal solution, with the object of deducing the heat of the reaction by means of van't Hoff's equation, $d \log K/dT = -Q/RT^2$.

The results of the experiments with *p*-nitrobenzaldehyde and

acetic anhydride in ethereal solution, and in presence of ferric oxide or phosphoric oxide, show that these oxides merely alter the velocity with which the condition of equilibrium is reached, the reaction being thus catalytic.

The reactions without solvent were carried out in presence of a colloidal solution of phosphoric oxide in acetic anhydride; here, too, the results show that this condensing agent acts purely catalytically. The value of Q is 3·911 cal. and 9·247 cal. for the reactions with *o*- and *p*-nitrobenzaldehyde respectively. With the *meta*-compound, the solubility in acetic anhydride is very slight at low temperatures, and the values of the reaction constant obtained at higher temperatures are of about the same order of magnitude as the experimental error.

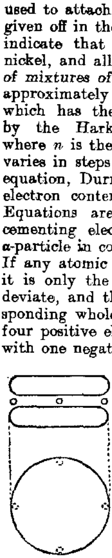
The probable mechanism of the action of colloidal solutions in these reactions is discussed (compare Duclaux, A., 1911, ii, 479; de Hemptinne, A., 1904, ii, 224; Burton, A., 1906, ii, 275; Perrin, A., 1905, ii, 138). T. H. P.

The Catalytic Decomposition of Hydrogen Peroxide by Colloidal Platinum. A. DE GREGORIO ROCASOLANO (*Compt. rend.*, 1920, **170**, 1502—1504).—Contrary to the conclusion of Bredig, it is shown that when electrosols of platinum are used, the decomposition of hydrogen peroxide by colloidal platinum is not a unimolecular reaction. During the reaction, the catalyst itself apparently undergoes some change. This altered catalyst will decompose further quantities of the peroxide, and the reaction is then unimolecular. W. G.

Annual Report of the International Committee on Atomic Weights for 1920–1921 (T., 1920, **117**, 885—888).

The Nuclei of Atoms and the New Periodic System. WILLIAM D. HARKINS (*Physical Rev.*, 1920, **15**, 73—94).—A summary and extension of previous papers on the nuclear structure of atoms. The data on which any theory of nuclear structure are based are atomic masses, atomic numbers which are assumed to be equal to nuclear charges, and atomic stabilities (given by the periods of disintegration when the atoms are radioactive), supposed by the author to be related to the relative abundance of the atomic species (elements) in nature. From these data, it is assumed (1) that all nuclei consist of positive electrons (or hydrogen nuclei $=\eta^+$) or eta particles, and negative electrons (β^-). Almost all of these are grouped in α^{++} particles or helium nuclei $=\eta_4{}^+\beta_2{}^-$; a few are grouped as mu particles ($\mu=\eta_3{}^+\beta_2{}^-$), both of which carry an even net charge; and a few as nu particles [$\nu=(\eta_3{}^+\beta_2{}^-)^+$], which have an odd charge, and are responsible for the existence of most atoms of odd atomic number, which are relatively rare. Thus, negative electrons almost always occur in pairs as binding electrons in these primary groups. Also pairs of cementing electrons are present in all heavy nuclei where they are

used to attach extra α-particles. Only the cementing electrons are given off in the disintegration of radio-atoms. The atomic weights indicate that chlorine, silicon, magnesium, neon, copper, zinc, nickel, and all elements with numbers from 28 to 80 (Hg), consist *of mixtures of isotopes. All atomic weights of atomic species* are approximately whole numbers, with the exception of hydrogen, which has the weight 1·0078. These whole numbers are given by the Harkins-Wilson equation, $W=2(N+n)+\frac{1}{2}+\frac{1}{2}(-1)^{N-1}$, where n is the number of cementing electrons in the nucleus, and varies in steps of 2 up to 26, which is the maximum. Using this equation, Durrant showed the normal plot for the cementing electron content of atoms. A simpler equation is $W=2(N+n)$. Equations are also *given for the number of α-particles and* cementing electrons in the nucleus. The atomic weight of the α-particle in complex nuclei is 4·000, as nearly as can now be told. *If* any atomic weights, except that of hydrogen, are not integers, it is only the atomic weights of the radioactive elements which deviate, and these may possibly be slightly higher than the corresponding whole numbers. The α-particle is assumed to consist of four positive electrons at the corners of a square lying in a plane, with one negative binding electron above and one below the plane.



The negative electrons are, with Rutherford, assumed to be relatively large, so that each one is close *to all four positive electrons. This* structure (see fig.) is assumed to be responsible for the difference in weight between the positive electrons and the α-particle. Nearly all elements are mixtures, so the term "atomic species" is proposed to indicate all atoms of one composition and structure. It is only the atomic weights of the atomic species which are whole numbers, since *most of the mixtures (elements)* are not in the proper proportion to give this result. An element may have an integer for an atomic weight if (1) it consists of one species, or (2) when only one isotope has a sufficient stability to make it evident in the atomic weights. The former is probably the case with such light atoms as oxygen, whilst the latter is true of the radioactive elements. Between atomic numbers 82 and 10 (possibly below this), is the region of stable isotopes. Two classes of isomeric atoms exist. (1) Non-isotopic isomerides, as UX_1, UX_2, and U_2, or $\alpha_{58}\mu\beta_{26}e'_{86}e_4$, $\alpha_{58}\mu\beta_{25}e'_{86}e_5$, and $\alpha_{58}\mu\beta_{24}e'_{86}e_6$, and (2) isotopic isomerides, which have the same nuclear composition. Here e represents a valence, and e' a *non-valence* planetary electron. Of the ordinary atoms, calcium and argon are isomeric, the difference in structure being due to the inclusion of two cementing electrons in the argon nucleus, which in calcium are present in the planetary system of non-nuclear electrons. The formulæ for the composition of the first twenty-seven elements and the radioactive elements are given, and it is possible to express radioactive changes by equations. Thus, $\alpha_{58}\mu\beta_{26}e'_{86}e_6$ is the

formula for uranium, $\alpha_{58}\beta_{26}e'_{86}e_4$ for thorium, $\alpha_{51}\mu\beta_{20}e'_{78}e_4$ for radio-lead, and $\alpha_{52}\beta_{22}e'_{78}e_4$ for thorium-lead. An alpha change is then indicated by the equation $\alpha_{58}\beta_{26}e'_{86}e_4 \longrightarrow \alpha_{57}\beta_{26}e'_{86}e_2 + \alpha^{++} + 2e^-$ (Th to meso-Th′), whilst a beta change is of the type $\alpha_{53}\mu\beta_{23}e'_{78}e_5 + e^- \longrightarrow \alpha_{53}\mu\beta_{22}e'_{78}e_6 + \beta^-$ (Ra-*C* to Ra-*C*′). In the nuclear structure of the light elements, the *v*-group ($\eta_3\beta_2$) occurs frequently, and is characteristic of the odd-numbered elements. Experiments proving that chlorine is a mixture of isotopes are nearing completion. These consist in a separation of chlorine into a lighter and a heavier fraction by diffusion.

CHEMICAL ABSTRACTS.

Electrons and Chemical Potential. FRED G. EDWARDS (*Chem. News*, 1920, **120**, 292—293).—A discussion of some points put forward by Henri (*Etudes de Photochimie*, Gauthier-Villars, Paris). The author derives the following statements from Henri's work. (1) Given the true graphic formula of any compound, the single bond represents one electron between the respective atoms. (2) The double bond appears when this single electron is withdrawn. The characteristic vibration is displaced towards the infrared by the consequent increase of mass in the vibrator, changing the speed of propagation and consequently the angle of dispersion. The three double bonds usually shown for benzene do not exist. (3) A triple bond appears when a second electron is similarly removed from the same pair of atoms. (4) A complete wavelength of incident light reciprocating with one electron of a molecule constitutes reciprocal absorption and emission. (5) An infrared half-wave-length ($E = h\nu$) absorbed by a molecule represents the addition of one electron. (6) An ultra-violet half-wave-length ($E_1 = h\nu_1$) absorbed represents the motion of an electron the distance of half a wave-length from one position in the molecule to another, and provides the mechanism of tautomerism. (7) There is a similar number of ultra-violet bands, the respective frequency of which is a large integral multiple of every respective infra-red band, the latter representing the total removal or replacement of an electron, but the former merely a rearrangement of its position in the molecule.

J. F. S.

An Electronic Theory of Isomerism. W. E. GARNER (*Nature*, 1920, **104**, 661—662).—The theory differentiates between two kinds of valency, according as the rotation of the electrons with respect to the valency is clockwise or anti-clockwise. Various types of isomerism (for example, eight possible isomerides of cinnamic acid) are discussed on the basis of this theory. All the isomerides, except the optical pairs, should possess different free energies, according to the arrangement of the rotating electrons.

J. R. P.

Space Filling and Ionic Mobility. RICHARD LORENZ (*Zeitsch. Elektrochem.*, 1920, **26**, 221—228).—A theoretical paper, in which

the relationships between the filling of space by the molecules an the ionic mobility are discussed. It is shown from these relation ships that the mobility may be calculated within limits from th space filling. This calculation is based on Stokes's formula applie to large ions, and it gives values for the molecular radii whic are of the correct order of magnitude. The molecular volume c the ions obtained in this way is compared with the molecula volume of the ion substance, and in the majority of cases it : found that the molecular volume of the ions (ϕ) is smaller tha the molecular volume of the ion substance (V_0). The term spac filling (ψ) is defined as the ratio of the space occupied by th molecules to that occupied by the mass of substance, and for th purpose of obtaining comparable results the last-named quantit is referred to absolute zero. The ratio is expressed by $\psi=\phi/V$ The space-filling figures can be calculated from the different theori of the equations of condition. The results are tabulated. Sinc the equations of condition are not absolutely definite, the spac filling is obtained as a value between two extremes, $0{\cdot}74>\psi>0{\cdot}2$ The space-filling values calculated from the ionic mobility all li between these two extremes. A table of values is given whic includes those for sixty univalent organic cations, thirty-seven un valent organic anions, six bivalent organic cations, and thirtee complex inorganic salts. This relationship constitutes electr conductivity as a branch of experimental atomistics. The exper mental space-filling values correspond approximately with the spac filling in cubic packing. The equations of condition of Sutherlan and Reinganum correspond most closely with the requirements c the present work. The ψ-curves obtained are shown to represer a first approximation only. Ions with normal space-filling numbe cannot be hydrated. J. F. S.

Theory of Electrolytic Ions. XV. Space-filling an the Mobility of Univalent Organic Anions. RICHARD LORE (*Zeitsch. anorg. Chem.*, 1920, **111**, 148—150. Compare A., 191 ii, 212, 262, 264; this vol., ii, 410).—The univalent organic anio bear a different relationship between the space filling and th mobility than do the cations (*loc. cit.*). The volume of the io substance (V_0) is analogous to that in the case of the cation $V_0=\sigma\times z$, where σ is the stere (5·75) and z is the number of ator in the ion. The molecular volume of the ion ϕ, and the volun of the ion substance V_0, give the space-filling numbers ψ, accordi to the equation $\phi/V_0=\psi$. J. F. S.

Structure of Matter and the Quantum Theory. F. H LORING (*Chem. News*, 1920, **120**, 291; **121**, 2—3).—Suppl mentary notes to the author's previous paper (this vol., ii, 365 The table previously given is completed up to, and includin nickel. J. F. S.

Experiments with a New Micro-balance. HANS PETTERSS((*Proc. Physical Soc.*, 1920, **32**, 209—221).—The balance is whol

of quartz, the usual knife-edge support being replaced by a pair of quartz fibres. Magnetic arrestment is employed, and balance obtained by displacement of a bulb at different pressures of air or magnetically. The range of weighings depends on the size of the beam; with one 5 cm. in length, the maximum load is 100—200 mg., and the setting can be made to within 10^{-7} mg.

J. R. P.

Use of Acetylene as a Source of Heat in Chemical Laboratories. NAUMANN (*Zeitsch. angew. Chem.*, 1920, **33**, i, 148).—Acetylene is readily generated from calcium carbide, and when burnt in a specially constructed Bunsen burner yields a very hot, non-luminous flame. W. P. S.

Explosion Accident at the Chemical Institute, University of Munster i.W., and Its Cause. R. SCHENCK (*Zeitsch. angew. Chem.*, 1920, **33**, ii, 245; *Chem. Zeit.*, 1920, **44**, 497).—During a lecture experiment to show combustion by combined oxygen, in which a mixture of toluene and tetranitromethane was being burnt, a violent explosion occurred, by which some thirty people were more or less injured. The cause of the explosion lay in the faulty preparation of the mixture. The correct quantities for safe burning are 67·5 c.c. of tetranitromethane (D 1·65) and 7·5 c.c. of toluene (D 0·8), but in place of this 67·5 grams of tetranitromethane and 7·5 grams of toluene had been taken, that is, the relative proportion of toluene was doubled. J. F. S.

Inorganic Chemistry.

Reaction between Hydrogen Peroxide and Peracids. A. RIUS Y MIRÓ (*Anal. Fis. Quim.*, 1920, **18**, 35—42).—It is shown that hydrogen peroxide, previously proposed as a reagent for hydroperoxides (this vol., ii, 368), reduces peracids of the types RO_2R and RO_2H. The author repeated the experiments of Riesenfeld (A., 1905, ii, 825; 1909, i, 963; ii, 951; 1910, ii, 51), according to whom perchromic acid has the formula H_3CrO_8; but, instead of 5 mols. of oxygen evolved per mol. of dichromate (thus, $2CrO_8''' + 12H^{\cdot} = 2Cr^{\cdot\cdot\cdot} + 6H_2O + 5O_2$), he found 4·6 to 6·5, which he explains by assuming the formation of Caro's acid. The author did not measure the evolved oxygen, but determined the amount of undecomposed hydrogen peroxide with permanganate, after adding the dichromate through a burette to the mechanically agitated acid solution of hydrogen peroxide. The oxygen evolved was found to be 3·71 to 4·33 mols. per mol. of dichromate. The greater evolution of oxygen corresponded with a low acidity.

because peracids are hydrolysed in acid solutions. The highest values must be due to the formation of an unstable higher perchromic acid. The ethereal solution of perchromic acid is gradually decomposed by hydrogen peroxide. Permonophosphoric, pervanadic, and perbenzoic acids are also acted on by hydrogen peroxide. W. R. S.

Preparation of Hydrogen Chloride from Chlorine and Water. H. D. GIBBS (*J. Ind. Eng. Chem.*, 1920, **12**, 538—541.)—By a reversal of the Deacon process, hydrogen chloride may be produced from chlorine and water with the employment of charcoal as a catalyst. The speed of the reaction is governed by the temperature, the relative concentrations of water and chlorine, and the character of the charcoal. For temperatures of 0°, 12°, 25°, and 37·5°, with a charcoal layer of 10 cm. depth and 10·75 sq. cm. cross-section, weight 67 grams, and mesh 8 to 10 per in.; a gas velocity of 500 cm. per min.; air–chlorine ratio, 500:1; water content of air, 50% saturation; pressure of gas above charcoal, 1 atm., and below, 1 atm. less 0·85 cm. water, the curves of production, after the initial rise, gradually flatten. Under the same conditions, but at a temperature of 25°, with water content of 0, 20, 40, and 80% saturation, and ratios of water to chlorine of 0:1, 3:1, 6·2:1, and 12·4:1, the curves indicate that the production of hydrogen chloride in each case reaches a constant rate dependent on the amount of water present. With two varieties of charcoal, a maximum hydrogen chloride production of 34%, falling off to 18% after 800 mins., and of 26%, falling to 7%, was obtained. W. J. W.

The Chemical Nature of Sulphur Chloride [Sulphur Dichloride]. MAX BERGMANN and IGNAZ BLOCH (*Ber.*, 1920, **53** [*B*], 977—979).—The preparation of the trisulphides of benzoic and anisic acids in 70—90% yield by the action of sulphur chloride on the potassium salts of the necessary thio-acid (this vol., i, 548) is of peculiar interest, since the chloride behaves as a definite chemical substance, SCl_2. The individuality of the compound has, however, been frequently doubted, and it has been regarded as a solution of chlorine or of chlorine and sulphur tetrachloride in sulphur chloride. Were this the case, the action of potassium thiobenzoate on it should yield a mixture of benzoyl di- and tetrasulphides, which might possibly be mistaken analytically for the trisulphide. Examination of molar mixtures of the compounds, however, shows that their physical behaviour is quite unlike that of benzoyl trisulphide, so that there is no possibility of confusion. The experiments therefore confirm the individuality of the chloride which has previously been shown to be probable by determination of molecular weight. H. W.

Production and Utilisation of Sulphur Dichloride. (SIR WILLIAM JACKSON POPE and CHARLES THOMAS HEYCOCK (Brit. Pat. 142879).—The employment of 1% by weight of finely

wdered absorbent charcoal as a catalyst greatly facilitates the action between chlorine and sulphur monochloride, and similarly, ien sulphur dichloride is subjected to conditions which lead to decomposition into chlorine and the monochloride, recombination is facilitated by similar means. G. F. M.

Arsenic-free Sulphuric Acid. K. SCHERINGA (*Pharm. Weekblad*, 1920, **57**, 421—422).—The greater part of the arsenic may be removed by heating the acid, after the addition of a little sulphite, so that some vapour is given off continuously. The acid is then diluted with an equal volume of water and electrolysed for at least one day. W. S. M.

Absorption of Nitrogen Oxides by Dilute Nitric Acid. ERIC K. RIDEAL (*J. Ind. Eng. Chem.*, 1920, **12**, 531—538).—The absorption of nitrogen dioxide by dilute nitric acid in presence of air was investigated with 10, 5, and 1% NO_2–air mixtures with nitric acid containing 50, 25, 10, and 8% HNO_3 at temperatures of 30°, 40°, and 50°, and the results are plotted on curves. Absorption in strong nitric acid proceeds most rapidly at low temperatures, but with water the reverse occurs. The point of inversion, that is, where absorption is independent of temperature, is reached with approximately 10% nitric acid. The limitation of the nitric acid concentration to 64% in absorption towers is caused by reduction of nitric acid by the nitrogen trioxide produced. The equilibrium constant of $2HNO_3 + N_2O_3 \rightleftharpoons H_2O + N_2O_4$ at ordinary temperatures is $K = 0{\cdot}81$. By agitation with oxygen, the N_2O_3 is converted into NO_2, and a higher strength of nitric acid is obtained, and by cooling a 12% NO_2–air mixture to 20° to remove excess of water above that required for the equation $2N_2O_4 + 2H_2O + O_2 = 3HNO_3$, and then refrigerating to $-10°$, nitric acid of 61·2—78·1% HNO_3 was produced. W. J. W.

Pressure Measurements of Corrosive Gases. The Vapour Pressure of Nitrogen Pentoxide. FARRINGTON DANIELS and ARTHUR C. BRIGHT (*J. Amer. Chem. Soc.*, 1920, **42**, 1131—1141).—An apparatus is described whereby the pressure of corrosive gases may be measured to a fraction of a millimetre. The essential part of the apparatus is a glass diaphragm, 1 cm. diameter and 0·1—0·2 mm. thick, made by flattening the bottom of a small bulb. The flat place and a short length of the stem are thickly coated with platinum, a glass arm with a rounded end, also platinised, is fused to the tube a short distance below the platinum coat, and bent twice at right angles, so that the rounded end just touches the flattened diaphragm, thus making an electrical contact between them. The arm and diaphragm are connected by means of platinum wires with a low-voltage cell and a galvanometer. The diaphragm is mounted in the apparatus containing the corrosive gas, so that the underside comes in contact with the gas, whilst the top is in contact with a variable air

pressure, which can be measured. Changes of pressure deflect the diaphragm and break the circuit, so that it is comparatively simple to see when the pressure of the gas under investigation is exactly balanced by a measured air pressure. This manometer has been used to determine the vapour pressure of nitrogen pentoxide at temperatures 243·0—305·5° abs. Nitrogen pentoxide was prepared by placing 25 c.c. of 100% nitric acid in a glass-stoppered wash-bottle and mixing with small quantities of phosphorus pentoxide until a thick paste was obtained. The mixture was kept in ice and salt during the mixing. The bottle was then connected with a U-tube containing phosphoric oxide, a second empty U-tube immersed in ice and salt to collect the pentoxide, and a protecting U-tube of phosphoric oxide. The mixture was warmed to 35—40°, and the system of tubes subjected to intermittent exhaustion. In this way, 5—10 grams of crude nitrogen pentoxide were condensed in two hours. The nitrogen pentoxide was purified by sublimation in a current of dry ozonised air, and condensed as a colourless, crystalline mass in the experimental tubes. All measurements of vapour pressure were made in the dark, and, since nitrogen pentoxide rapidly decomposes in the gaseous state, an estimation of the rate of decomposition was made at each temperature, and the vapour pressure corrected for this. The vapour pressure of nitrogen pentoxide is represented by the empirical formula $\log P_{mm} = 1244/T + 34{\cdot}1 \log T - 85{\cdot}929$, which is more in keeping with the experimental results than the formula of Russ and Pokorny (*Monatsh.*, 1913, **34**, 1027). The experimentally determined values are closely in agreement with those of Russ and Pokorny. The following values were obtained: 258° abs., 13 mm.; 263° abs., 21 mm.; 268° abs., 32 mm.; 273° abs., 51 mm.; 278° abs., 79 mm.; 283° abs., 118 mm.; 288° abs., 183 mm.; 293° abs., 279 mm.; 298° abs., 420 mm.; 303° abs., 620 mm.; 305·5° abs., 760 mm. The heat of sublimation has been calculated for various temperatures; the following values are obtained for various absolute temperatures: 263°, 12,360 cals.; 268°, 12,640; 273°, 12,760; 278°, 13,110; 283°, 13,360; 288°, 14,160; 293°, 14,140; 298°, 14,040.

J. F. S.

The Transition from Coal to Coke. ERIC SINKINSON (T., 1920, **117**, 839—843).

The Oxidation of Coals. MARCEL GODCHOT (*Compt. rend.*, 1920, **171**, 32—34).—The coal used was divided into two fractions by extraction with pyridine. The original coal gained 3·15% by weight by oxidation in one month at 100°. The extract and the residue after extraction only gained, under similar conditions, 1·22% and 1·99% respectively, whereas when the coal was reconstructed by mixing extract and residue together, this mixture gained 3·20%. The theory of bacterial action in the oxidation of coal is scarcely in accord with these results, as any such bacteria would have been destroyed during the extraction with pyridine.

W. G.

The Electromotive Activity of Carbon Monoxide. III. K. A. HOFMANN (*Ber.*, 1920, **53**, [*B*], 914—921. Compare A., 1916, ii, 637; 1919, ii, 23).—The present communication deals with he reactions involved in the oxidation of carbon monoxide at opper surfaces moistened with alkali.

It is found that carbon monoxide is slowly oxidised in open ircuit, the electrolyte ultimately containing, in addition to arbonate, traces of formate and scarcely any oxalate; the monxide is gradually replaced by hydrogen, so that the reaction roceeds according to the scheme: $CO + 2KOH = K_2CO_3 + H_2$. In he closed circuit, the hydrogen is oxidised to water by oxygen iberated at the opposite electrode. Copper cannot, however, bring aseous molecular hydrogen into a condition of electromotive ctivity, but can be very actively charged by nascent hydrogen, nost simply by cathodic polarisation.

It appears probable that carbon monoxide, owing to the existnce of subsidiary valencies, has the power to unite with alkali ydroxide in the presence of copper to yield small amounts of an oformate, Cu . . . C(OH)(OK), which then combines with a urther molecule of the hydroxide to yield the alkali carbonate, hilst the hydrogen is liberated in the atomic state at the copper. his conception is supported by the observation that active lements are not formed from copper, carbon monoxide, and water, r from carbon monoxide and alkali hydroxide alone, but only rom copper, alkali hydroxide, and carbon monoxide in conjuncion. It is further found that hydrated cupric oxide is only educed by carbon monoxide in the presence of alkali at an appreciable rate if a certain amount of metallic copper is present. Again, he electromotive activity of carbon monoxide at a copper, and to less degree at a platinum, surface is not immediately developed, hilst, in the absence of hydroxyl ions, carbon monoxide is not oticeably activated by copper. Cuprous oxide does not play a art in the phenomena, since it is found that hydrated cupric xide is directly reduced in the presence of alkali to the metal, hilst the presence of a minute amount of oxygen diminishes the lectromotive force of the system Cu–CO–alkali in a striking, if ransitory, manner. H. W.

Revision of the Atomic Weight of Silicon. Analysis f Silicon Tetrachloride. GREGORY P. BAXTER, PHILIP F. EATHERILL, and EDWARD O. HOLMES, jun. (*J. Amer. Chem. oc.*, 1920, **42**, 1194—1197).—The atomic weight of silicon has een determined from the analysis of silicon tetrachloride. The trachloride was prepared by the action of chlorine on silicon, ltered to remove ferric chloride, and then kept in contact with ercury for a week in an exhausted flask to remove excess of lorine. The clear liquid was then carefully fractionated at low mperatures by the method previously described by Baxter and arkweather for tin tetrachloride (this vol., ii, 436), and sealed to a series of small bulbs. The more volatile portions, which obably contain hydrogen chloride, and the less volatile portions,

which probably contain silicon hexachloride, titanium tetrachlorid
and carbon tetrachloride, were rejected. The bulb was weighe
and broken under a solution of chloride-free sodium hydroxid
the solution was acidified with nitric acid and precipitated wit
about the correct amount of pure silver nitrate solution of know
concentration, and the end-point determined by means of
nephelometer. As a mean of four experiments, the rati
$SiCl_4:4Ag=0{\cdot}393815$, whence the atomic weight of silicon
28·111 (Cl = 35·457, Ag = 107·880). J. F. S.

Helium: its Production and Uses. A Lecture Delivere before the Chemical Society on June 17th, 1920. JOH CUNNINGHAM MCLENNAN (T., 1920, **117**, 923—947).

Helium in Brannerite. ROGER C. WELLS (*J. Franklin Inst* 1920, **189**, 779—780; *Chem. News*, 1920, **121**, 22).—The g liberated when brannerite (this vol., ii, 257) is fused with hydroge sodium sulphate was found, spectroscopically, to contain helium.
L. J. S.

Continuous Flow Apparatus for the Purification Impure Helium Mixtures. E. EDWARDS and R. T. ELWORTH (*Trans. Roy. Soc. Canada*, 1919, **13**, [iii], 47—52).—Helium cor taining at least 12% of impurity can readily be purified by passin it in a continuous stream over charcoal at the temperature liquid air or oxygen. The rate of flow can be increased to at lea 10 litres per hour without decreasing the efficiency of the proces The maximum rate of flow was not determined. By the use of tw or more sets of charcoal tubes in parallel, the process may be ma continuous, as the charcoal may be revivified without disturbi the flow. J. R. P.

Combustibility of Mixtures of Hydrogen and Heliun JOHN SATTERLY and E. F. BURTON (*Trans. Roy. Soc. Canada*, 191 **13**, [iii], 211—215).—The combustibility was tested by a light match and by a white-hot platinum spiral. Under the conditio of experiment, the percentage of hydrogen could be raised to before the mixture became inflammable; if the percentage exceede 28, the mixture would burn. J. R. P.

Formation and Decomposition of Sodium Hypochlorit F. GIORDANI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1919, [iii], **2** 138—153).—Investigation of the action of chlorine on solutions sodium hydroxide under different conditions shows that the prima action consists in the formation of sodium hypochlorite, and followed by decomposition of the latter, with formation of chlora and chloride and liberation of oxygen. The distribution betwe these two reactions of the active chlorine, which disappears, depen notably on the illumination, the temperature, the concentratio of free sodium hydroxide, and the nature of the vessel, and possib on other factors.

he formation of hypochlorite is accompanied by increase in ıme, which must be taken into account in calculating the amount odium hydroxide required to yield hypochlorite of definite titre. 'he concentration of the free sodium hydroxide in the product rts a marked influence on the stability. Contrary to Lunge's erpretation ("Sulphuric Acid and Alkali," Vol III, 1911), of .elle and Descosses' results (*Mon. Sci.*, 1903, 624), perfectly ıtral sodium hypochlorite solution is not stable, but undergoes id decomposition. In practice, the action is best arrested when solution contains 1·5% of sodium hydroxide.

The statement that the law, according to which the percentage omposition of the hypochlorite per unit time varies with the centration, is not in agreement with theoretical considerations erroneous. T. H. P.

The Arsenites of Lithium and Potassium. F. A. H. CHREINEMAKERS and (MLLE) W. C. DE BAAT (*Rec. trav. chim.*, 920, **39**, 423—428).—A study of the ternary system, lithium cide–arsenious oxide–water, at 25° shows the existence of one senite $LiAsO_2$, which is soluble in water without decomposition. . similar study shows that potassium gives two arsenites, $K_2As_4O_7$ nd $K_6As_4O_9,12H_2O$, both of which are soluble in water without ecomposition. W. G.

Crystal Structure of Cæsium Dichloro-iodide. RALPH V. G. WYCKOFF (*J. Amer. Chem. Soc.*, 1920, **42**, 1100—1116).—Cæsium dichloro-iodide has been stated to crystallise in two forms, hombic and hexagonal (rhombohedral). The rhombohedral form s obtained by dissolving 10 grams of cæsium chloride in 50 c.c. of water, adding 8 grams of iodine, and passing chlorine through the hot solution until the iodine has dissolved. On cooling slowly, six-sided plates, about 1 cm. diam. and less than 1mm. thick, are formed. All attempts to prepare the rhombic variety failed. When the method recommended by Wells and Penfield (A., 1892, 773) was used, crystals were obtained which appeared to be rhombic, but, when examined by the *X*-rays, the pattern indicated that they were twinned, and on breaking the crystals, they were frequently found to be hollow. The density of the rhombohedral form is found to be 3·86. The structure of the crystals was obtained from the *X*-ray spectrum obtained from the anticathode of an *X*-ray bulb, using the crystal as a grating, and from a study of the Laue patterns obtained by passing *X*-rays through a section of the crystal. It is shown that the body centred unit rhombohedron contains one molecule. The cæsium atom is placed either at the centre or the corner of this unit, and the iodine atom either at the corner or the centre. Two chlorine atoms lie on the long diagonal very close to 0·31 of its length from the corners. Because of the supposedly very nearly equal scattering power of cæsium and iodine, it is impossible at present to decide between the two possibilities. J. F. S.

Additive Compounds of Ammonia with Ammonium Haloids. JAMES KENDALL and J. G. DAVIDSON (*J. Amer. Chem. Soc.*, 1920, **42**, 1141—1145).—The freezing-point curves of the ammonium haloids with ammonia have been determined over the whole available composition range. It is shown that in the case of ammonium fluoride, no compounds are formed, and that this substance is practically insoluble in liquid ammonia. In the other cases, the following compounds are shown to exist, $NH_4Cl,3NH_3$, m. p. 10·7°; $NH_4Br,3NH_3$, m. p. 13·7°; $NH_4I,3NH_3$, m. p. −8·0°; and $NH_4I,4NH_3$, m. p. −5·1°. Other compounds of these systems previously recorded were not observed, and in all probability do not exist. The stability of the additive compounds with ammonia increases regularly as the series of the ammonium haloids is ascended, and it is therefore held to be likely that some of these compounds may be capable of existence in the vapour phase.

J. F. S.

Some Reactions started by a Primer. ERNEST BERGER (*Compt. rend.*, 1920, **170**, 1492—1494).—Numerous reactions, when started by localised heating, will spread throughout the whole mass. The priming mixture suggested by the author consists of sixty parts of potassium nitrate or sodium nitrate and forty parts of industrial calcium silicide. This mixture can be lit with a match, and its combustion produces a very high temperature. It has been used to start such reactions as the reduction of boron phosphate or arsenate by aluminium, the reduction of calcium or barium sulphate by red phosphorus, the preparation of silicon and boron fluorides from lead fluoride. W. G.

Production of Chlorides by Primed Reactions. ERNEST BERGER (*Compt. rend.*, 1920, **171**, 29—32. Compare preceding abstract).—Aluminium will replace a number of metals and metalloids from their chlorides by spontaneous action or by a primed reaction. In some cases, magnesium is still more active. In the same way, a considerable number of metals, such as calcium, magnesium, aluminium, manganese, *etc.*, will displace the carbon from organic chlorides, such as carbon tetrachloride, tetra- and hexa-chloroethane, and chloroform. Such actions, when started, continue with the generation of a considerable amount of heat, the metallic chloride being vaporised. In the case of liquid organic chlorides, these may first be absorbed in kieselguhr or sawdust. Such mixtures found application in the production of smoke clouds during the war. W. G.

Complex Salt Formation. E. H. RIESENFELD and H. FELD (*Zeitsch. Elektrochem.*, 1920, **26**, 286—288).—A solution of barium sulphate in 90% sulphuric acid has been electrolysed between platinum electrodes by a current of 190 milliamperes and 440 volts. After the current had passed for seven and a-half hours, the change in concentration in the anode and cathode cells was determined.

The results show that the barium migrates to the anode as a complex ion, and that in consequence the compound usually termed barium hydrogen sulphate must be regarded as a complex acid of the formula $H_2[Ba(SO_4)_2]$. Similar experiments were carried out with a solution of silver chloride in 35% hydrochloric acid, and it was found that here also a complex acid of the formula $H[AgCl_2]$ is present. J. F. S.

Experimental Determination of the Vapour Pressure Curves of Molten Cadmium and Zinc, and the Calculation of the Chemical Constants of Cadmium, Zinc and Monatomic Bromine. H. BRAUNE (*Zeitsch. anorg. Chem.*, 1920, **111**, 109—147).—The vapour pressure of molten cadmium and zinc has been determined for small pressures (up to 79 mm.) by the circulation method, and for pressures up to 2 atms. by the boiling-point method. The results are represented by the equations, $\log p = -5763/T - 1\cdot28 \log T + 12\cdot282$ for cadmium, and $\log p = -6655/T - 1\cdot147 \log T + 12\cdot046$ for zinc. The specific heats of the molten metals have been determined over a considerable range of temperature. The atomic heats calculated from the specific heats are practically constant over the temperature range between the melting point and the boiling point. The values found are: cadmium 7·50, zinc 7·24. The chemical constant of both elements was calculated from the vapour-pressure measurements, and the values $1\cdot54 \pm 0\cdot2$ for cadmium and $1\cdot11 \pm 0\cdot7$ for zinc obtained, which are in keeping with theory for the chemical constants of monatomic gases. The chemical constant of monatomic bromine has been determined from Bodenstein's measurements of the dissociation of bromine (A., 1916, ii, 552). The calculation could not be strictly carried out because of lack of information on the specific heat of bromine at low temperatures; nevertheless, the values obtained are shown not to be at variance with the theory of the chemical constants of monatomic gases. J. F. S.

The Transmutation of Simple Substances. LAURENT NAUDIN (*Mon. Sci.*, 1920, [v], **10**, 121—122).—A very brief account of unpublished experiments of Schützenberger, in which he found that, when lead, carefully purified from silver, was chlorinated by chlorine gas and subsequently reduced by hydrogen at a high temperature, the lead then contained traces of silver. This process was repeated several times on the same sample of lead, carefully purified between each process, always with the same results.

W. G.

Formation of the Autogenous Lead-tree. A. THIEL (*Ber.*, 1920, **53**, [*B*], 1066—1072).—It has been shown by Senderens that a lead-tree is formed when the metal is immersed in solutions of certain lead salts, and the phenomenon has been explained by Cohen and Helderman (A., 1915, ii, 456) on the basis of the presumed allotropic forms of lead. Since the author has shown, how-

ever, that lead does not form allotropes (following abstract), thi explanation is no longer tenable. Crystallographical examinatior of autogenous and other lead-trees, of electrolytic lead, and o solidified lead shows the crystals to be invariably of the sam type and to be composed of combinations of octahedron and cube The formation of the autogenous tree occurs uniformly unde acidified solutions of lead nitrate, but very seldom (in two case out of fifty) under Heller's solution. The explanation is to b found in the author's theory of desglomeration (followin abstract). Local ionic concentration systems are set up in th interstices between the crystallites as the nitrate solution penetrate into them, and becomes exhausted without the possibility of fre admixture with the external, less exhausted solution. There ar thus formed short-circuited ionic concentration cells, thus:

Metallic short
circuit

External solution | + Lead − Internal solution

Electrolytic conductivity in the liquid channel.

in consequence of which the lead-tree becomes developed a irregular positions over the whole surface of the metal. Wit Heller's solution, the tendency towards the formation of such cell is much less pronounced, since under the most favourable condition the potential developed does not exceed 10 millivolts, whilst wit the nitrate solutions it may even exceed 40 millivolts. H. W.

The supposed Allotropy of Lead. A. Thiel (*Ber.*, 192 **53**, [*B*], 1052—1066).—It has been shown by Heller (A., 191 ii, 634) that compact lead ultimately crumbles to a powder whe preserved beneath acidified solutions of lead salts, and the phen menon has been attributed to allotropic change. The results, an also the nature of the product, have been confirmed by Cohen an Heldermann (A., 1915, ii, 456), who, however, consider that sever allotropes are formed. The author's experiments, on the oth hand, lead him to the conclusion that the phenomenon is not d to allotropy, but to simple chemical action.

The majority of the experiments were performed with sampl of commercial soft lead containing about 0·005% of iron, and n other impurity in detectable amount. In consequence of th difficulties regarding the supply of gas, they were generally effect at the ordinary temperature, about 18°, although at times th temperature fell as low as 0°. In conformity with Heller's sol tion (molar with respect to lead acetate and 0·4*N* with respect nitric acid), the solutions were, in general, molar as regards lea salt and 0·4*N* as regards acid. Strips of lead weighing 8— grams, which had previously been repeatedly etched by dilu nitric acid, were immersed in about 10 c.c. of the necessa solutions.

The disintegration of lead is only observed in solutions whi

contain nitrate ions, and does not occur, for example, with lead acetate and acetic acid, lead chloride and hydrochloric acid, lead nitrite, lead silicofluoride and hydrofluosilicic acid, lead perchlorate and perchloric acid. Disintegration which has been started in specimens of lead by Heller's solution is arrested when hey are transferred to nitrate-free solutions. Lead is slowly ittacked when immersed in Heller's solution, nitrogen and nitric xide being evolved, and the metal being considerably dissolved revious to the commencement of the stage at which it begins to all to powder. Similarly, the metal is attacked by solution of itrates which are free from lead; reaction, however, starts more lowly, so that it would appear that the process is catalysed by the resence of lead ions or lead nitrite.

Further evidence against the theory of the formation of an llotrope of lead is afforded by inspection of the disintegrated pro-uct, which is found to consist of homogeneous, irregularly poly-edral granules with more or less rounded edges; these are, in eneral, relatively large in size and free from small crystals, such s would be expected if a new modification had been formed. gain, according to Cohen and Heldermann, the transition mperature lies at about 50° (60° according to Jänecke), above hich the compact modification is stable; it is found, however, that ad rapidly disintegrates under Heller's or other solution contain-g nitrate at 100°, although unaffected under these conditions in idified lead acetate and lead perchlorate solutions. Lastly, only very slight difference of potential is observed between compact d disintegrated lead immersed in lead perchlorate solution.

The author explains the phenomenon in the following manner. ompact lead is composed of crystallites, the crevices of which are led by a finely granular eutectic, which is present even in "pure" etals (a similar structure must be assumed for all metals which ve solidified from the molten state). This eutectic is more adily attacked by a suitable agent when the impurities are re chemically active than the metal itself; in consequence, cavi-s are formed around the crystallites, which finally become so ep that the latter are completely detached from the main mass. he term "disglomeration" is proposed for the phenomenon.) support of this hypothesis, it is shown that disintegration can o be effected by other suitable agents, as, for example, when a d anode slowly dissolves in a solution of perchloric acid, although action is less marked in this case. On the other hand, dis-meration is only to be expected when dealing with solidified tals, and it is interesting to note that lead crystals, in the form the lead-tree, are only resolved into the individual crystals when nersed in hot or cold Heller's solution, whilst, further, massive d can be protected from disintegration by coating it with a osit of electrolytic lead. Attempts are also described to find er instances of disglomeration, and it is shown that copper can disintegrated by immersion in ammoniacal persulphate solution.

H. W.

The Composition of Ancient Eastern Bronzes. MASUMI CHIKASHIGE (*T.*, 1920, **117**, 917—922).

Colloidal Cuprous Oxide. C. PAAL (*Zeitsch. anal. Chem.*, 1920, **59**, 166—167).—Referring to a method described by Ruoss (A., 1919, ii, 367) for the preparation of colloidal cuprous oxide, the author points out that the substance has been known for some considerable time (compare A., 1906, ii, 356, 358; 1914, ii, 656).

W. P. S.

The Precipitation of Mercuric Salts by Hydrogen Sulphide. PIERRE JOLIBOIS and PIERRE BOUVIER (*Compt. rend.*, 1920, **170**, 1497—1498).—Using the apparatus previously described (this vol., ii, 107, 112) to study the action of varying proportions of hydrogen sulphide on mercuric chloride in dilute solution, it is shown that the black precipitate, formed with excess of hydrogen sulphide, has the composition HgS, and the white precipitate, formed in the presence of excess of mercuric chloride, has the composition $2HgS,HgCl_2$. There is no indication of the existence of any other intermediate compound. W. G.

Corrosion of Iron. R. KATTWINKEL (*Zeitsch. angew. Chem.*, 1920, **33**, i, 156).—An incrustation which formed in a steam pipe had strong magnetic properties, and consisted almost entirely (99·12%) of magnetic iron oxide, Fe_3O_4. W. P. S.

Action of Metallurgical Additions on the Anomaly of the Dilatability of Nickel Steels. CH. ED. GUILLAUME (*Compt. rend.*, 1920, **170**, 1433—1435).—A detailed study of the action of manganese, chromium, and carbon on the dilatability of nickel steels over the range of easily obtainable alloys, and of a series of nickel steels containing 5% of copper. The addition of any of these third constituents diminishes the intensity of the anomaly of dilatability in the region of its minimum value. In the case of manganese, carbon, and copper, within a limited region of nickel content, ternary alloys are obtained which are slightly less dilatable than the binary alloys with the same nickel content.

If the other constituents are well known, the measurement of the dilatability gives a method of fixing the carbon content to within 1 in 10,000. W. G.

Values of the Dilatabilities of Nickel Steels. CH. ED. GUILLAUME (*Compt. rend.*, 1920, **170**, 1554—1557. Compare preceding abstract).—Using nickel steels containing 0·4% of manganese and 0·1% of carbon, the true dilatabilities first decrease to a minimum as the nickel content increases, and then increase again. The minimum value of the dilatability, a_{20} $1·19 \times 10^{-6}$, corresponds with a nickel content of 35·6%. Allowing for the coefficients of dilatability of manganese and carbon, it is shown that such an alloy of pure iron and nickel would have a dilatability equal to $0·2 \times 10^{-6}$. W. G.

Thermal Change of the Elastic Properties of Nickel Steels. P. CHEVENARD (*Compt. rend.*, 1920, **170**, 1499—1502).—A study of the anomaly of elasticity of twenty-eight nickel steels containing varying proportions of nickel and only just the amount of manganese indispensable to forging. The method employed was to measure the time and decrement of oscillation of a torsion pendulum constructed with wires of the steels.

The coefficient of variation of the modulus of torsion is characterised, in reversible alloys, by a rapid increase to a maximum, which corresponds with the minimum of dilatability, and then a gradual diminution. For alloys with a stable state in the cold, the results do not indicate any irregularity.

Tempering and hammer hardening diminish the value of the modulus of torsion, which increases, however, with the temperature of annealing, there being a maximum of rapidity between 450° and 550°.

As in the case of the dilatability, the thermo-elastic coefficient is affected by the treatment which the alloy undergoes. Contrary to what happens in the case of the dilatability, however, hammer hardening diminishes the amplitude of the anomaly, whilst tempering increases it. W. G.

The Constitution of the Lilac-grey Complex Chromium Sulphate. A. RECOURA (*Compt. rend.*, 1920, **170**, 1494—1497).—The lilac-grey chromium sulphate previously described (this vol., ii, 114) consists of one molecule of the green chromium sulphate and two molecules of the normal violet sulphate. When freshly prepared, the SO_4'' ions corresponding with the green sulphate are masked, whilst the SO_4'' ions corresponding with the violet salt are precipitable. On keeping, the latter SO_4'' ions also become masked. The explanation given is that in the freshly-precipitated lilac-grey salt the green sulphate is in its depolymerised state, but, once solid, it rapidly and spontaneously becomes converted into its polymerised form, and in this form is capable of masking the SO_4'' ions of the violet salt. W. G.

Bromination of Antimony in Ethereal Medium. A. RAYNAUD (*Bull. Soc. chim.*, 1920, [iv], **27**, 411—414).—When an excess of dry bromine is added to finely powdered antimony in dry ethyl ether and the liquid boiled for three hours, a crystalline *compound*, having the composition $SbBr_5,OEt_2$, is obtained. When freshly prepared, it does not fume in air, but is decomposed by water. The ether is only removed by heating the compound at 55°. When exposed on a porous plate in a bell-jar over sulphuric acid, the compound is, in a few days, converted into antimony tribromide. W. G.

Mineralogical Chemistry.

Graphite in Japan. SEIJIRŌ NODA (*Beitr. Min. Japan*, 1915, No. 5, 260—261).—The various modes of occurrence and origin are briefly discussed. The following analyses show that the scaly graphite from crystalline rocks contains more carbon and less volatile matter than the compact graphite from metamorphosed sedimentary rocks (of Palæozoic and Mesozoic age):

Rock Matrix.	C.	S.	Volatile matter.	H_2O.	Ash.
Gneiss	88·87	trace	1·86	0·53	8·74
Granite	58·00	trace	2·22	0·40	39·38
Palæozoic	20·85	0·44	7·40	0·49	71·24
Mesozoic	1·36	0·03	6·72	0·42	91·50

L. J. S.

Tetrahedrite from Besshi Mines, Prov. Iyo, Japan. KOTOJIRŌ ARAI (*Beitr. Min. Japan*, 1915, No. 5, 267—268).—Analysis by K. ISHII gave:

Cu.	Sb.	As.	Bi.	S.	Fe.	Ag.
33·672	30·538	0·227	0·139	26·789	4·424	0·487

Au.	Mn.	Ni.	Co.	SiO_2.	Al_2O_3.	CaO.	MgO.
0·0005	0·007	0·007	trace	1·052	1·48	0·30	0·66

Mercury, zinc, lead, and tin are absent. L. J. S.

Calcite Deposit from the Senami Hot Spring, Japan. DENZŌ SATŌ (*Beitr. Min. Japan*, 1915, No. 5, 281—282).—From a boring made in prospecting for oil at this locality, water at a temperature of 100° gushed out to a height of 20 metres, and the oil concession became a spa. A snow-white, crystalline crust is deposited by the water, and the pipe and conduit have frequently to be cleared. The water is clear and colourless, neutral in reaction, and slightly alkaline in taste, D^{14} 1·0035. Analysis gave, in grams per litre:

K.	Na.	Ca.	Mg.	Cl.
0·0786	1·3333	0·1323	0·0003	2·1162

SO_4	H_2CO_3	H_2SiO_3.	CO_2.	Total.
0·2759	0·0632	0·1928	0·1596	4·3522

Analysis I is of the lower layer, with a slight grey tinge, and II of the colourless, transparent upper layer. D 2·72. Rhombohedra of calcite, with curved faces, are present in the drusy portions:

	CaO.	MgO.	MnO.	$Fe_2O_3+Al_2O_3$.	SiO_2.	CO_2.	H_2O.	Total.
I ...	55·14	trace	0·35	0·50	0·36	43·25	0·32	99·92
II .	55·57	—	0·29	0·27	0·14	43·65	0·30	100·22

L. J. S.

Aragonite Cones formed at the Kuriyama Geysers, Prov. Shimotsuke, Japan. WATARU WATANABE (*Beitr. Min. Japan*, 1915, No. 5, 237—241).—Hot (94°) water, with a sulphurous odour, issuing from rock crevices gave, on analysis by M. KAWAKITA (grams per litre):

NaCl.	$HNaCO_3$.	$CaCO_3$.	Na_2SO_4.	K_2SO_4.	$MgCO_3$, $MnCO_3$, $FeCO_3$.
1·1642	0.1241	0·1600	0·1134	0·0531	*traces*

D^{21} 1·02. The water has an alkaline reaction after boiling. The material of the aragonite cones deposited by this water gave, on analysis by Y. ŌSHIMA:

$CaCO_3$.	$SrCO_3$.	$BaCO_3$.	$MnCO_3$.	$Fe_2O_3+Al_2O_3$.	Insol.*	Total.
93·26	0·65	0·50	0·99	1·32	3·12	99·84

* *Consisting chiefly of free sulphur and some organic matter.*

The interior of the cones consists of calcite, and the central channel through which the water passes is lined with pink crystals of mangano-calcite. A cone, measuring 30 cm. across the base, 30 cm. high, and weighing 13·878 kilos., was formed around an orifice during a period of ten months; and when it was broken off, another cone grew in its place. Some extinct geyser cones at another district in Japan reach a height of 4 metres; these are now transformed into calcite. The hot springs deposit volatile sulphides, such as orpiment, realgar, and cinnabar. L. J. S.

Calcareous Deposit from Hot Spring Water at Hokuto, Formosa. KOTORA JIMBŌ (*Beitr. Min. Japan*, 1915, No. 5, 283).—In reservoirs of the hot water, calcium carbonate is deposited as minute, irregular, disk-shaped aggregates of very fine acicular crystals. The deposit is brown in colour, and gave, on analysis by SAEGI:

CaO.	SrO.	Al_2O_3.	Fe_2O_3.	MgO.	CO_2.	Ign.
38·74	trace	0·39	6·29	0·86	43·63	3·81

L. J. S.

Refractive Indices of the Rhombohedral Carbonates. P. GAUBERT (*Bull. soc. franç. min.*, 1919, **42**, 88—120).—The observed values of the refractive indices of isomorphous mixtures of these carbonates agree closely with those calculated from their chemical composition by the formulæ of Mallard. The following method for distinguishing magnesite from the other carbonates is given: The powdered sample is heated to a red heat and a drop of cobalt nitrate solution is added, after cooling. A bluish-green halo immediately develops around particles of all carbonates except magnesite. CHEMICAL ABSTRACTS.

Wolframite (Ferberite and Hübnerite) from Japan. KOTORA JIMBŌ (*Beitr. Min. Japan*, 1915, No. 5, 256—259).—Scheelite occurs with rock-crystal in quartz veins at Kurasawa,

Kai. It is sometimes replaced by brownish-black ferberite (anal. I), these pseudomorphs having been originally described as tetragonal iron tungstate under the name "reinite." Microscopic crystals of hair-brown to dark red hübnerite (anal. II) occur with scheelite in gold-quartz at Nishizawa.

	WO_3.	FeO.	MnO.	CaO.	MgO.	Total.
I	75·214	24·372	0·185	—	—	99·771
II	*74·25*	*3·18*	*20·84*	*1·01*	*trace*	99·28

L. J. S.

Thaumasite and Spurrite from California. W. F. Foshag (*Amer. Min.*, 1920, **5**, 80—81).—Small needles of thaumasite form interlaced masses and fibrous veins in a rock composed of åkermanite and spurrite (A., 1909, ii, 61) in the crystalline limestones at Crestmore, California (A., 1919, ii, 113). Analysis gave:

SiO_2.	$(Al,Fe)_2O_3$.	CaO.	SO_3.	H_2O+CO_2(ign.).	Total.
9·10	0·84	12·98	27·56	49·48	99·96

The spurrite shows polysynthetic twinning, and is optically negative with α 1·638, β 1·676. Since the rock contains 4·64% CO_2, it follows that spurrite forms half the mass. Thaumasite has evidently been derived from spurrite by the action of sulphated waters, although sulphates are rare in the deposit. L. J. S.

Mineralogy of Korea (Chōsen). Nobuyo Fukuchi (*Beitr. Min. Japan*, 1915, No. 5, 207—227).—Sixty mineral species are described. Yellow to brown crystals of orthoclase with a violet-blue schiller (moonstone) from Sōzen gave K_2O 6·43, Na_2O 6·53%, D 2·60. Crystals of zircon from Jidō gave SiO_2 33·06, ZrO_2 63·32, Fe_2O_3 3·33, TiO_2 nil; total, 99·71. The material is colourless, but it shows a dark violet on the surface and along cracks. Several partial analyses are given of phlogopite, ranging from MgO 23·77, FeO 1·47% in the colourless variety to MgO 4·52, FeO 3·45% in the black. L. J. S.

Crystalline Nodules in Agalmatolite from Mitsuishi, Japan. Hideyuki Awazu (*Beitr. Min. Japan*, 1915, No. 5, 298—299).—The minute crystals composing the nodules are colourless with a perfect cleavage, and are doubtfully referred to gibbsite. [The following analysis suggests, however, that the material consists of diaspore with intermixed opal, as described by Y. Chitani (*J. Geol. Soc. Tokyo*, 1915, **22**, 384; see *Mineralogical Abstracts*, 1920, **1**, 64).]

Al_2O_3.	Fe_2O_3.	CaO.	MgO.	CO_2.	SiO_2.	H_2O.	Total.
70·43	0·32	0·01	0·03	0·35	14·37	14·38	99·89

L. J. S.

Analcite from Maze, Japan. Seigo Shimizu (*Beitr. Min. Japan*, 1915, No. 5, 295).—The following analysis agrees with the formula $Na_2O,Al_2O_3,4SiO_2,2H_2O$:

SiO_2.	Al_2O_3.	FeO.	MgO.	CaO.	K_2O.	Na_2O.	H_2O.	Total.
54·58	23·05	nil	0·10	0·45	nil	13·50	8·70	100·38

L. J. S.

Axinite Crystals from Japan. MASAAKI HOSHINA (*Beitr. Min. Japan*, 1915, No. 5, 294—295).—Pale violet-grey axinite, forming with quartz the gangue of copper ores at Ogiyama, gave:

SiO_2.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	Ign.
45·20	15·61	6·84	6·33	22·80	0·82	0·32

L. J. S.

Chlorite from Jōdoyama, Japan. DENZŌ SATŌ (*Beitr. Min. Japan*, 1915, No. 5, 296—298).—Loose blocks occurring on the surface of the granite-gneiss mountain of Jōdoyama consist of an aggregate of garnet, quartz, calcite, and dark green chlorite. The last of these gave on analysis:

SiO_2.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	Ign.	Total.	Sp. gr.
30·12	11·80	35·22	3·29	5·81	3·58	10·27	100·09	3·25

L. J. S.

Epidote Crystals from Katakai, Japan. KINZŌ NAKASHIMA (*Beitr. Min. Japan*, 1915, No. 5, 253—255).—Large, brownish-green to greyish-green crystals embedded in massive, milky quartz gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	H_2O.	Total.
38·34	27·45	8·81	0·86	0·21	23·21	0·31	2·21	101·40

L. J. S.

Diabantite, Stilpnomelane, and Chalcodite from Westfield, Massachusetts. EARL V. SHANNON (*Proc. U.S. Nat. Mus.*, 1920, **57**, 397—403).—The diabase exposed in the trap quarries of this district is more or less altered with the formation of dark green, earthy, chloritic decomposition products. These are usually not sufficiently pure for chemical investigation, but better material was obtained from certain fissures. I is the mean of four analyses of diabantite. This is dark green and clayey when wet, but on drying it shrinks and cracks to a friable, pale olive-green mass. D 2·77. The minute micaceous scales are optically negative and sensibly uniaxial. Heated in the closed tube, it becomes brown, yields neutral water, and finally fuses to a black, magnetic glass. It is readily soluble in hot hydrochloric or sulphuric acid, and less easily in nitric acid, in each case with the separation of flocculent silica. II is the mean of two analyses of stilpnomelane obtained from another fissure, but with the same general appearance as the diabantite; it is, however, more blue, more plastic, has a peculiar sub-metallic lustre, and the dried material is compact and tough. The two minerals can be distinguished by their behaviour in boiling nitric acid (D 1·20). Diabantite dissolves slowly without change, whilst stilpnomelane is wholly oxidised, yielding a rust-like, brown material. Analysis III is of chalcodite, which is found only in small amount as a scaly coating with a rich golden-yellow colour and metallic lustre. A minute amount

of pure material contained SiO_2 45·77%, with much ferric iron, no ferrous iron, and very little alumina and magnesia. This is evidently an indefinite oxidation product of stilpnomelane; in some cases it still showed a green core containing ferrous iron.

	SiO_2.	Al_2O_3.	Fe_2O_3	FeO.	MnO.	CaO.	MgO.	H_2O (at 105°).	H_2O (>105°).	Total.
I.	28·15	15·17	3·85	25·23	0·21	0·59	14·56	0·57	11·25	99·58
II.	44·08	4·74	5·27	23·31	0·87	trace	8·36	2·21	10·28	99·12
III.	44·64	6·75	23·59	—	—	—	—	6·21	7·14	98·19

L. J. S.

The Cumberland Falls (Whitley Co., Kentucky) Meteorite. GEORGE P. MERRILL, with analyses by EARL V. SHANNON (*Proc. U.S. Nat. Mus.*, 1920, **57**, 97—105).—This stone, which fell on April 9th, 1919 (this vol., ii, 47), represents a new type of meteorite, for which the name *Whitleyite* is suggested. It is a coarse breccia consisting of a chalky-white to grey portion in larger amount, with enclosed angular blocks of a black chondritic stone. The two portions each represent different types of stones, and the whole mass shows much evidence of crushing and distortion. The lighter-coloured portion (bulk analysis I) consists mainly of enstatite intimately intergrown with a monoclinic pyroxene, and with small quantities of diallage, nickel-iron, troilite, and graphite. The dark portion (bulk analysis II) owes its colour to finely-disseminated graphite and metallic particles:

	SiO_2.	Al_2O_3.	Cr_2O_3.	P_2O_5.	FeO.	NiO.
I............	55·172	0·382	0·062	trace	2·916	0·123
II............	41·683	1·537	0·591	trace	9·399	0·211
	CoO.	CaO.	MgO.	MnO.	Na_2O.	K_2O.
I............	trace	1·586	38·734	0·112	0·157	0·150
II............	trace	4·059	27·848	—	trace	trace
	Fe.	Ni.	Co.	Cu.	Mn.	Cr.
I............	0·888	0·059	0·004	0·003	0·005	trace
II............	12·108	0·747	0·078	0·001	0·088	trace
	S.	P.	Cl.	C.	H_2O.	Total (less O for Cl, S, P).
I............	0·784	0·034	0·028	0·164	0·167	100·961
II............	2·464	0·014	0·045	0·449	0·210	100·084

The percentage composition of the metallic portion of each is given under IA and IIA respectively:

	Fe.	Ni.	Co.	Mn.	Cu.	Cr.	Total.
IA.......	92·596	6·152	0·417	0·522	0·313	trace	100·000
IIA.......	92·982	5·735	0·599	0·076	0·008	trace	100·000

IB is of the friable, chalky-white enstatite (with intergrown monoclinic pyroxene), forming the main mass of the lighter portion. IIB of the silicate (22·582%), decomposed by dilute hydro

chloric acid; and IIc of the insoluble silicate (56·58%) in the darker portion:

	SiO_2.	Al_2O_3.	FeO.	NiO.	CoO.	MnO.	CaO.	MgO.	Ign.	Total.
I_s..	59·53	1·09	0·98	nil.	—	—	0·96	37·17	0·33	100·06
II_s..	38·239	trace	6·566	0·043	trace	0·709	5·246	49·197	—	100·000
II_i..	58·341	2·705	3·528	0·295	trace	0·562	5·073	29·496	—	100·000

From these analyses, the mineralogical composition of the dark enclosures is: metal, 13·022; troilite, 6·760; lawrencite, 0·080; chromite, 0·869; soluble silicates, mainly olivine, 22·582, insoluble silicates, mainly pyroxenes, 56·580; carbon, mainly amorphous, 0·449; calcium phosphate, trace; hygroscopic water, 0·210; total, 100·552. L. J. S.

Analytical Chemistry.

Filter with Perforated Plate and Wire Gauze. F. Mach and P. Lederle (*Chem. Zeit.*, 1919, **43**, 831).—Silver gauze may be used in place of platinum in the filter described previously by the authors (A., 1919, ii, 303). W. P. S.

Iron Basins and their Use in Analysis. H. Sertz (*Zeitsch. angew. Chem.*, 1920, **33**, i, 156).—Iron basins are useful for sulphide fusions, particularly when they have been treated previously with nitric acid. W. P. S.

The Alteration of Glass Flasks used in Laboratories. R. Dubrisay (*Bull. Soc. chim.*, 1920, [iv], **27**, 409—411).—The physico-chemical volumetric method previously described (compare A., 1913, ii, 388) for the estimation of traces of alkali can be used for the estimation of the amount of alkali dissolved from glass vessels when water is boiled in them. The method has been applied to compare the resistance of some French flasks made during the war with that of some pre-war German flasks. The French flasks showed up very well, both in their resistance to attack by boiling water and by boiling alkali. W. G.

Methyl-orange as Indicator. V. Macri (*Boll. Chim. farm.*, 1920, **59**, 193—196).—The author describes the behaviour of methyl-orange in presence of various compounds which affect its action as an indicator (compare *J. Soc. Chem. Ind.*, 1920, August). T. H. P.

Use of Conductivity Titrations in Neutralisation Analysis. III. Titration of Combined Weak Acids or Bases in Salt (Displacement Curves). I. M. Kolthoff (*Zeitsch. anorg. Chem.*, 1920, **111**, 97—108. Compare A., 1919, ii, 74, 76).—The quantity of a weak acid or base combined as a salt may

be estimated by titration with a strong base or acid, respectively, using the electrical conductivity as indicator. On adding a strong acid, say, hydrochloric acid, to the salt of a weak acid, the weak acid will be displaced, and, having a low degree of ionisation, the conductivity of the solution will change very little, but as soon as all the weak acid has been liberated, the first drop of strong acid in excess will cause a great increase in the conductivity. On plotting the conductivity against the number of c.c. of standard acid, a sharp break will be found, which represents the point of equivalence. The method is found to work well in all cases where, after displacement of 50% of the weak acid, the conductivity has not increased more than 1%. Examples are given of the titration of sodium acetate, sodium formate, and for weak bases, ammonium chloride. In the case of the dibasic acids in sodium oxalate, sodium tartrate, and sodium citrate, it is found that good results may be obtained here also, if in the last-named two cases an equal volume of alcohol is added to the solution before titration.

J. F. S.

Spectrophotometric Study of the "Salt Effects" of Phosphates on the Colour of Phenolsulphonthalein Salts and some Biological Applications. CHARLES L. BRIGHTMAN, M. R. MEACHEM, and S. F. ACREE (*J. Bact.*, 1920, **5**, 169—180. Compare A., 1919, ii, 75).—Phosphate solutions, varying in concentration from $0.5N$ downwards and showing the same hydrogen-ion concentration by the hydrogen electrode method, have a marked influence on the colour of phenolsulphonthalein salts. This salt effect becomes small when the phosphate concentration is $0.05N$ or less. The apparent ionisation constant of the phenolic group of the phenolsulphonthaleins varies with the concentration of the phosphate present, and averages about 2.65×10^{-8} when uncorrected for salt effect. When a graphic method is used for calculating the ionisation constant freed from the salt effect of phosphate, the value is lowered to about 1.95×10^{-8}.

CHEMICAL ABSTRACTS.

Improved Form of McLeod Gauge. AUSTIN BAILEY (*Chem. News*, 1920, **120**, 302).—A modification of the McLeod gauge, which consists mainly of a three-way tap which connects the mercury reservoir with either an aspirator or the air through a fine jet, and of a movable and interchangeable pressure chamber which permits of the gauze being used over large ranges of pressure. With this apparatus, the danger of the mercury rising too rapidly into the pressure chamber is avoided, because the air can only enter through the fine jet. J. F. S.

A Weight Burette for Gas Analysis. E. R. WEAVER and P. G. LEDIG (*J. Amer. Chem. Soc.*, 1920, **42**, 1177—1185).—A weight burette is described for use in gas analysis. By means of

this, the volume of the sample and changes in volume after absorption of constituents are determined by weighing the quantity of mercury, after compensation, which is expelled from, or taken into, the burette. It is claimed that, with this device, the volumes obtained are very accurate, and the accuracy of the measurement is independent of the state of the meniscus. The readings are quite free from parallax errors, since no graduated scales have to be read. The gas to be measured never comes in contact with a stopcock, rubber tube, or other possible origin of a leak. The apparatus may be made of any desired size. A number of measurements are recorded, and it is shown that the average deviation from the mean value in a single gas estimation is 0·0044%, whilst the maximum divergence is only 0·014%.

J. F. S.

Theory of the Katharometer. H. A. DAYNES and G. A. SHAKESPEAR (*Proc. Roy. Soc.*, 1920, *A*, **97**, 273—286).—The katharometer is an instrument designed for automatic registration of small quantities of hydrogen (1%—2%) in air; it is also of considerable use in determining the permeability of balloon fabric to hydrogen. In the present paper, an account is given of the instrument, and this is followed by a theoretical treatment of the principles involved in the use of the instrument. The instrument consists of two small helices of thin platinum wire (ca. 0·001 inch diam.) enclosed each in one of two cells in a copper block; each helix is mounted in a small frame consisting of a loop of copper wire soldered to a ring of copper. This ring is fitted with an insulating plug, through which the copper lead wire is introduced. One extremity of the helix is soldered to the lead and the other to the distal end of the loop. The outer part of the lead passes through a plug of rubber fitting into the cell, and over this rubber an ebonite plug is pressed down by a screw collar. Thus the cell is rendered gas-tight. Both cells are similarly fitted, except that, whilst one is hermetically sealed, the other communicates with the atmosphere by three small holes. The helices constitute two arms of a Wheatstone bridge, and have a resistance of about 8 ohms. The main working current of the bridge is 0·100 ampere, and this gives the wires a temperature about 15° above that of the copper block. Contact with hydrogen, owing to surface combustion, raises the temperature of one helix, and from the change in resistance the amount of hydrogen in the air may be estimated.

J. F. S.

Titration of certain Chlorides with Silver Nitrate, using Potassium Chromate as Indicator. H. W. BOLAM (*Chem. News*, 1920, **120**, 292).—When barium, or other metal yielding a chromate less soluble than silver chromate, is present, slightly more chromate than is sufficient to precipitate the barium should be added before proceeding with the titration of a chloride with silver nitrate.

W. P. S.

Gravimetric Analysis. XIII. Estimation of Sulphuric Acid. III. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1920, **33**, 159—160, 162—163. Compare this vol., ii, 329).—Tables are given showing the corrections to be applied to the weight of barium sulphate precipitates for the effect of alkali chlorides and other salts on the precipitation. The presence of ammonium chloride decreases the effect of other salts.

A summary is given of conditions of precipitation, and of corrections to be applied, as detailed in the earlier parts, in order to obtain trustworthy results. W. P. S.

Estimation of Nitro-groups by a Modification of Young and Swain's Method. LOUIS DESVERGNES (*Ann. Chim. anal.*, 1920, [ii], **2**, 141—143).—Many nitro-substances, when dissolved in sodium hydroxide solution, yield a brown coloration, which interferes with the iodometric estimation of the excess of stannous chloride used in Young and Swain's reduction method (A., 1898, ii, 186); it is therefore recommended that alcohol be used for dissolving the substance. The alcoholic solution is heated for two hours with an excess of stannous chloride solution in an atmosphere of carbon dioxide, and the excess is titrated subsequently with iodine solution. The method is trustworthy with a large number of nitro-substances, but not so in the case of nitrophenols and nitronaphthalenes. W. P. S.

Apparatus for the Estimation of Nitric Nitrogen by Devada's Method. JOSEPH ERLICH (*Ann. Chim. anal.*, 1920, [ii], **2**, 143—153).—The apparatus consists of a flask in which the nitrate is reduced by means of Devada's alloy, a condenser, and a receiver. The flask is connected with the condenser by a bulbed tube containing glass balls to prevent spray passing over into the receiver; a tube extends down the centre of this bulbed tube, and is used for passing a current of air through the apparatus towards the end of the operation. W. P. S.

Colour Changes of the Diphenylamine Reaction. E. M. HARVEY (*J. Amer. Chem. Soc.*, 1920, **42**, 1245—1247).—A modified diphenylamine reagent for use in microchemical tests for nitrates consists of 0·05 gram of diphenylamine, 7·5 c.c. of sulphuric acid (95—96%), 2·5 c.c. of 10% aqueous potassium chloride solution; or, if it is particularly desirable to avoid darkening of tissue, 5 c.c. of sulphuric acid, 3 c.c. of glacial acetic acid, and 2 c.c. of 12% aqueous potassium chloride solution may be used, at some sacrifice of colour intensity. A diagram shows that over the ranges 0—41%, 41—46%, 46—83%, 83—87%, 87—100%, with maxima of intensity at 38%, 71%, and 100% of sulphuric acid, the colours observed are oriental green to yellow, bluish-green, blue, colourless, and purple, respectively. The proportion of diphenylamine is variable between fairly wide limits, but in excess it interferes with the reaction; variations of temperature between 20° and 50°

have little effect; potassium chloride causes not only an intensification of the blue colour, but an extension in both directions of the concentrations of sulphuric acid which produce it, and it is more suitable for this purpose than sodium chloride, owing to the greater solubility of its acid sulphate. The stability of the blue colour once produced, even in concentrations of acid in which normally it would not be produced, renders the order of mixing of some importance. J. K.

Denigès's Strychnine-Molybdate Reaction. L. Débourdeaux (*Bull. sci. pharmacol.*, 1920, **27**, 70—72).—In order to detect phosphates in the presence of barium, the preparation of Denigès' strychnine-molybdate reagent has been modified as follows: Strychnine (1·17 grams) is dissolved on a boiling water-bath in 200 c.c. of water and 8 c.c. of nitric acid (1:9). Ammonium molybdate (75 grams) is dissolved in 50 c.c. of water, the solution is mixed while cold with 50 c.c. of nitric acid (D 1·20), digested at 40° for four days, and the clear solution decanted or filtered through glasswool. Thirty c.c. of this solution and 30 c.c. of nitric acid (1:9) are added to the strychnine nitrate solution, and the whole is made up to 300 c.c. The reagent thus prepared is at first colourless, but acquires finally the colour of picric acid, at which point it has reached its maximal sensitiveness. This occurs about the eighth or tenth day, although the reagent can be used on the third day. The sensitiveness persists for two to three months, but only 1% remains after five to six months. The sensitiveness depends largely on the molybdate solution, which must be freshly prepared as described. CHEMICAL ABSTRACTS.

Estimation of Small Amounts of Phosphoric Acid as Barium Phosphomolybdate in the Presence and in the Absence of Phosphorus in Organic Combination. S. Posternak (*Bull. Soc. chim.*, 1920, [iv], **27**, 507—518).—It is possible to estimate amounts of phosphorus as small as 0·05 mg. by precipitation and weighing as barium phosphomolybdate from the corresponding ammonium salt in a medium containing, in addition, only sulphate alone or nitrate alone.

In the absence of organic matter, the inorganic phosphorus is precipitated from hot solution in the presence of 5% of sulphuric acid and 10% of ammonium sulphate. The ammonium phosphomolybdate precipitate is washed four times with a 5% solution of ammonium nitrate, then dissolved in a little ammonia, and reprecipitated with a 10% solution of barium chloride. The precipitate is collected, washed with water, dried, and calcined at a red heat. It has the constitution $4Ba_{27}[PO_4(MoO_4)_{12}]_2,Ba_9[SO_4(MoO_4)_6]$, and its weight when multiplied by 0·00739 gives the weight of phosphorus present.

In the presence of organic compounds of phosphorus, the inorganic phosphorus is first precipitated at 15° in a medium containing at least 5% of ammonium nitrate. The precipitate of

barium phosphomolybdate finally obtained in this case has the constitution $8Ba_{27}[PO_4(MoO_4)_{12}]_2,Ba_4(MoO_4)_4$, and the factor for converting its weight into weight of phosphorus is 0·00786. Under these conditions, none of the organic phosphorus is precipitated.

W. G.

Presence of Phosphates in Human Blood. X. The Nephelometry of Phosphoric Acid in Analyses which deal with Quantities of the Order of Magnitude employed in Bang's Method as a Means of Studying the Distribution of Phosphorus, especially in Lecithinæmia. JOH. FEIGL (*Biochem. Zeitsch.*, 1920, **102**, 131—141).—A detailed discussion of the technique of the above method. S. S. Z.

Some Quick Methods for [the Detection of] Arsenic and Antimony. CHAS. W. CUNO (*Proc. S. Dakota Acad. Sci.*, 1919, **3**, 34—47).—The following methods are sensitive to 0·1%. (1) The substances in acid solution are precipitated by hydrogen sulphide, the precipitate is well washed and extracted several times with an ammoniacal solution of ammonium carbonate to remove arsenic sulphide, which is then reprecipitated by concentrated hydrochloric acid; copper interferes very little if the precipitate has been well washed. Antimony sulphide is removed from the precipitate by repeated washing with a hot solution of sodium carbonate; by using small quantities and re-heating each time, the antimony is obtained in concentrated solution, and separates, on cooling, almost quantitatively at 0°. Tin is removed from the sulphide precipitate by sodium hydroxide solution, and is detected in the usual way.

(2) When copper and mercury are not present, a solution of the ore in hydrochloric acid is treated with sodium thiosulphate, whereby arsenic, antimony, and bismuth are precipitated, but not cadmium and tin. The precipitate is boiled with concentrated hydrochloric acid, when the arsenic remains undissolved. When arsenic, antimony, tin, copper, cadmium, and bismuth are all present, the material is dissolved in hydrochloric acid, and the solution is warmed with a concentrated solution of sodium thiosulphate, whereby arsenic only is precipitated, together with some sulphur; by diluting the solution to six volumes and warming, antimony will first appear as a red coloration, which is quickly masked by the other metals.

(3) When copper is absent, arsenic can be detected by dissolving the substance in concentrated hydrochloric acid and passing a rapid stream of hydrogen sulphide into the concentrated solution; no other metal except copper is precipitated in concentrated hydrochloric acid solution. CHEMICAL ABSTRACTS.

Estimation of Small Quantities of Arsenic. K. SCHERINGA (*Pharm. Weekblad*, 1920, **57**, 420—421).—A slight modification in the Bloemendal arsenic apparatus is described. The estimation

of arsenic in urine is carried out as follows: 500 c.c. of urine are evaporated to dryness with 30 grams of pure sodium chloride. The residue is transferred to a distillation flask, and 30 c.c. of pure concentrated sulphuric acid are added. As much as possible of the hydrogen chloride is distilled over and is absorbed in 100 c.c. of saturated sodium carbonate solution. To the solution, a slight excess of bromine is added, and then 5 c.c. of 10% sodium phosphate solution and 5 c.c. of ammoniacal magnesia mixture. The precipitate is dissolved in dilute sulphuric acid, reduced, and the solution transferred to the apparatus. This procedure is applicable to most organic substances containing arsenic. W. S. M.

Rapid Estimation of Arsenic in Commercial Sulphuric Acid. A. A. Kohr (*J. Ind. Eng. Chem.*, 1920, **12**, 580—581).—For the estimation of arsenious arsenic, 20 grams of acid are diluted with water, and a few drops of methyl-orange added. The solution is neutralised with sodium carbonate solution until it is very faintly pink, and about 2 grams of powdered sodium hydrogen carbonate are then added. The solution, after dilution with water to 250 c.c., is titrated with $0{\cdot}1N$-iodine and starch, a blank test being made. For determining the arsenic in the arsenic form, 20 grams of acid are heated for one hour in an oven at 105—110°. It is then diluted with a little water, and a saturated solution of sodium hydrogen carbonate added in slight excess, phenolphthalein being used as indicator. The solution is boiled and filtered. Three grams of powdered sodium hydrogen carbonate are added, and 150 c.c. of hydrochloric are slowly poured in with agitation, after which 1 gram of potassium iodide is added, and air excluded. After agitation and remaining for five minutes, the solution is titrated with $0{\cdot}1N$-thiosulphate and starch. The reaction, $H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2HI$, proceeds from left to right when the concentration of the hydrogen ion is low; and there should be few OH ions. In presence of sufficient hydrogen chloride, the reaction goes from right to left. Copper salts interfere in the arsenic determination but are usually negligible. If in appreciable amount, they must be estimated, and a correction applied to the thiosulphate titration. W. J. W.

The Acidimetric Estimation of Boric Acid. J. A. M. van Liempt (*Zeitsch. anorg. Chem.*, 1920, **111**, 151—166).—See this vol., ii, 331.

Estimation of Carbon Dioxide in Moorland Waters. V. Rodt (*Chem. Zeit.*, 1920, **44**, 469).—In titrating the free carbon dioxide and that present as hydrogen carbonates in moorland waters, errors are caused by the presence of weak organic acids and their salts, which are simultaneously titrated. Winkler's method (*Zeitsch. Nahr. Genussm.*, 1910, **20**, 617) of removing free carbon dioxide by repeatedly spraying the water would scarcely be applicable on a small scale. When the solvent action of moorland

a fireclay crucible, a covering layer of 25 grams of borax glass being added. The mass is fused in a muffle for twenty minutes. The lead is then separated from the slag and weighed, the factor 0·0872 giving the equivalent aluminium. A high temperature should be employed to reduce the time of fusion and minimise re-oxidation of the lead. W. J. W.

A Method for the Determination of the Ion Concentration in Ultra Filtrates and other Protein-free Solutions. R. BRINKMAN and (MISS) E. VAN DAM (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 762—771).—A simple method for measuring the concentration of calcium ions in a solution of a mixture of salts is based on the following principle. To a solution containing $Ca^{··}$, there are added oxalate ions until the solubility of calcium oxalate is just reached. A slight milkiness appears directly this point is passed. The method is correct to 2—3 mg. of calcium per litre. The principle of the method can be applied to the estimation of other ions. The only condition is the employment of a reagent that will give a very sparingly soluble salt with the ion the concentration of which is to be measured. J. C. D.

Colorimetric Method for the Estimation of the Copper and Iron Present in Lead and Lead Oxides. CHARLES R. HARDY (*Chem. News*, 1920, **120**, 256).—A rapid method of estimating small quantities of iron and copper in metallic lead or litharge. The sample (200 grams) is dissolved in nitric acid (D 1·2) and diluted as the action proceeds to prevent lead nitrate crystallising. The solution is treated with concentrated sulphuric acid (32 c.c. per 100 grams of sample) and the precipitate allowed to settle. The solution is decanted four or five times, treated with 10 c.c. of sulphuric acid, and evaporated nearly to dryness. After cooling, the liquid is diluted with water and filtered. The filtrate is evaporated to small bulk, treated with a few drops of nitric acid, boiled and treated with ammonia. The precipitate is filtered, redissolved, and reprecipitated. The filtrates from the iron contain all the copper; these are evaporated and the volume made up to 50 c.c. The measured quantity is made ammoniacal and boiled until quite neutral. When cold, the solution is placed in a Nessler glass, 5 c.c. of potassium ferrocyanide solution (0·4%), and 5 c.c. of ammonium nitrate solution (10%) added. In a second Nessler glass, 5 c.c. of ferrocyanide and 5 c.c. of ammonium nitrate are placed, and the volume made the same as that in the first glass with distilled water. A standard solution of copper (0·393 gram $CuSO_4,5H_2O$ per litre) is added from a burette until the colour in both glasses is the same.

The iron precipitate is dissolved in a small quantity of nitric acid and made up to 250 c.c.; 25 c.c. is placed in a Nessler glass with 9 c.c. of 25% hydrochloric acid and 5 c.c. of ammonium thiocyanate solution (5%). In a second glass, 10 c.c. of 25% hydrochloric acid and 5 c.c. of thiocyanate solution are placed, and the volume made up to that in the first glass. A standard iron solu-

tion (0·210 grams ferrous ammonium sulphate per litre) is then run in from a burette until the tints of both are alike.

If red lead has to be examined, a 20-gram sample should be taken, dissolved in aqua regia, and sufficient water added to dissolve all the lead chloride. J. F. S.

Assay of Alunite. EDWARD S. SIMPSON (*Chem. Eng. Min. Rev. Australia*, 1919, **11**, 297—298).—The estimation of the total alunite is based on the fact that alunite is the only sulphate in the ore which is insoluble in water, but soluble in dilute sodium hydroxide solution; not uncommonly, a little calcium and magnesium sulphates are present, for which a correction must be made. Sulphates soluble in water are estimated by treating 0·7 to 0·8 gram of the ore with 100 c.c. of water, and after one hour estimating the dissolved sulphates as barium sulphate. Total sulphates are estimated by heating 0·7 to 0·8 gram of the ore with 60 c.c. of 5% sodium hydroxide solution on the steam-bath for one hour, with occasional stirring, and estimating the sulphate in the filtrate as barium sulphate. From the total sulphate are subtracted the sulphate found in a blank experiment and the water-soluble sulphate; the difference, expressed as a percentage of the ore and multiplied by 2·55, gives the percentage of alunite (including natro-alunite). The error may be $+2\%$.

The estimation of the extractable alkali oxides in the ore is performed by heating 0·5 to 0·6 gram of the ore in a muffle furnace at 819° during one hour (freshly fused sodium chloride is used to indicate the temperature; the temperature must not exceed 877° [m. p. of lead oxide]), and, after cooling and weighing, extracting the residue with boiling water and treating the filtrate with 7 c.c. of barium chloride solution (122 grams in a litre) and 0·6 gram of hydrated barium hydroxide; after removing the excess of barium and the calcium in the usual way, the total alkali chlorides and the potassium chloride (as platinichloride) are estimated by the usual methods. The results, corrected by the amounts found in a blank experiment, are expressed as percentages of the raw ore and of the roasted ore. CHEMICAL ABSTRACTS.

Rapid Volumetric Method for the Estimation of Iron, Applicable in the Presence of Hydrochloric Acid, Phosphorus, Oxy-acids, and Organic Matter. H. DROOP RICHMOND and EDITH M. ISON (*Analyst*, 1920, **45**, 258—260).—The following method gives trustworthy results for the estimation of iron in many pharmaceutical preparations. From 5 to 10 c.c. of the sample are treated with a few drops of hydrochloric acid, and $N/10$-permanganate solution is added until a transitory purple coloration is produced throughout the solution. An equal volume of concentrated hydrochloric acid is then added, followed by a small quantity of sodium hydrogen carbonate (to give an atmosphere of carbon dioxide), and $N/10$-stannous chloride solution is run in drop by drop until a drop of the mixture gives a blue

coloration with potassium ferricyanide solution. The mixture is then titrated with $N/10$-stannous chloride solution, using thiocyanate solution as an external indicator. The number of c.c. of $N/10$-stannous chloride solution used in the titration is multiplied by 0·0056 to obtain the quantity of iron present. W. P. S.

Estimation of Iron and Separation of Manganese from Iron by the Ammonium Salt of Nitrosophenylhydroxylamine (Cupferron). E. H. ARCHIBALD and RUTH V. FULTON (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 243—253).—The cupferron precipitate of iron is slightly soluble in the acid solution from which it is precipitated. The solubility is apparently not affected by the substitution of sulphuric for hydrochloric acid, but is appreciably lowered by adding ammonium chloride to the solution. The precipitate is slightly soluble in the wash-water. If corrections are applied for these solubilities, the method is very exact. Iron can be separated from manganese in a solution containing four times as much manganese as iron, the amount of manganese carried down by the precipitate being inappreciable for most purposes. The amount increases with the acid dilution of the mother liquor. The presence of ammonium chloride to the extent of 5 grams in 100 c.c. of solution is an advantage in the separation. J. R. P.

Use of the Rotating Zinc Reductor in the Estimation of Molybdenum. WALTER SCOTT (*J. Ind. Eng. Chem.*, 1920, **12**, 578—580).—The rate of reduction of molybdic acid by zinc is nearly as rapid between 20° and 30° as at the boiling point. Reduction is not appreciably affected by the aid of an electric current. By covering the beaker with a split cover-glass during the operation, enough hydrogen is retained to act as a protective covering for the zinc. The reduced solution may be titrated with permanganate in the same beaker; if it is transferred to another vessel, it must be poured into ferric alum and syrupy phosphoric acid. W. J. W.

Bibliography of the Analysis of Antimony. ELTON R. DARLING (*Chem. Eng.*, 1919, **27**, 11—12, 63; from *Chem. Zentr.*, 1919, ii, 890; 1920, ii, 750).—A compilation of English, French, and German literature on the subject. E. H. R.

Process for Testing Air for the Presence of Combustible Substances. E. BECKMANN [with KURT STEGLICH] (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1914, **34**, 924—936).—Two pieces of apparatus have been designed, primarily to test the air of coal mines in respect of explosibility due to the presence of methane. That for the preliminary test consists of a cylinder fitted with a piston and inlet valve for collection of the sample, which is exploded by means of pyrophoric iron, the heat generated causing a temporary expansion, which is registered by a manometer. A locking device ensures that the igniter shall not be operated until

the inlet valve is closed. Explosion only takes place when 7—10·3% of methane is present, but the limits can be widened somewhat by compression of the gas and by use of a catalyst, although its untrustworthiness renders the latter not very suitable for practical purposes. Addition of methane or air with the same object to samples outside the limits given is also liable in practice to lead to erroneous results. The second apparatus is a metal cylinder, containing potassium hydroxide, connected to a suction pump which serves to fill the vessel with air to be tested, and to a mercury manometer which indicates the contraction due to absorption of the carbon dioxide and water resulting from combustion of the methane. Ignition is secured by a platinum spiral, made white-hot by a current for the space of two minutes, the time being regulated by a mercury contact on the principle of the ordinary sand-glass. A non-return valve protects the manometer from the initial force of explosion, and provision is made for the automatic sounding of an electric alarm to follow a contraction due to a proportion of methane in excess of the safety limit. A determination takes about three minutes, and a form of the apparatus has been developed by which analyses are automatically made and registered every half-hour. As the gas examined is not filtered, any dust present exerts the same effect as it would do in an actual explosion. The explosions diminish in intensity with increase in the proportion of methane, and no longer occur when this reaches 16%. Further, in consequence of the increasing formation of carbon monoxide and hydrogen in these circumstances, the degree of contraction observed gradually diminishes and gives place to an expansion when 20% or more of methane is present. Any uncertainty as to the meaning of a small contraction is removed by repetition of the determination after admixture of air with the gas under examination. Hydrogen and illuminating gas may be detected by the first apparatus between limits of 9 and 42%, 8 and 25% respectively; further, the fact that a red heat suffices to initiate their combustion in the second apparatus supplies a means of detecting these gases in presence of methane. J. K.

Estimation of Acetylene in Coal Gas and Air by Means of Ilosvay's Reagent. H. Arnold, E. Möllney, and F. Zimmermann (*Ber.*, 1920, **53**, [*B*], 1034—1039. Compare Ilosvay de Nagy Ilosva, A., 1900, ii, 52).—The coal gas is shaken in a separating funnel of about 3 litres capacity with about 20 c.c. of the reagent at intervals during an hour; the precipitate is filtered and well washed with water containing hydroxylamine. The precipitate and filter are treated in a crucible with a little concentrated nitric acid, the solution is evaporated, and the residue ignited and weighed as copper oxide. The results obtained in this manner are sometimes high, due to the presence of impurities derived from the reagents in the precipitated copper acetylide, but this drawback may be overcome by dissolving the precipitate from the filter with nitric acid and evaporation of the filtrate.

Test analyses with mixtures of acetylene and air show the method

to be very accurate, and to be available even when not more than 0·04% of acetylene is present; at such dilutions, however, it is necessary to add about 5% of carbon dioxide to the mixture, since otherwise the results are low as a consequence of atmospheric oxidation. The process can also be used for the estimation of acetylene in coal gas, from which hydrogen sulphide, if present, must be removed; this can be effected by dry copper sulphate-pumice. H. W.

Volumetric Estimation of Acetylene. RICHARD WILLSTÄTTER and ERNST MASCHMANN (*Ber.*, 1920, **53**, [*B*], 939—941).—Methods of estimating acetylene, which are based on its reaction with silver nitrate and titration of the nitric acid liberated in accordance with the equation $C_2H_2 + 3AgNO_3 = C_2Ag_2,AgNO_3 + 2HNO_3$, are found to be untrustworthy, since it has not been found possible to find conditions under which a molecule of the gas liberates two molecules of nitric acid, the amounts of acid actually set free varying from about 0·5 mol. in alcoholic, to about 1 mol. in aqueous solution. The following procedure gives trustworthy results. Acetylene, in gaseous form or in solution, is agitated for a few minutes with Ilosvay's reagent freshly prepared from copper nitrate, ammonia, and hydroxylamine hydrochloride, and the precipitated copper acetylide is filtered through an asbestos filter and washed until the filtrate no longer decolourises *N*/10-permanganate, care being taken not to allow the precipitate to become dry. The copper acetylide is washed from the asbestos by means of about 25 c.c. of a solution prepared by making up ferric sulphate (100 grams) and concentrated sulphuric acid (200 grams) to a litre with water. The ferrous sulphate, formed in accordance with the equation $C_2Cu_2 + Fe_2(SO_4)_3 + H_2SO_4 = FeSO_4 + 2CuSO_4 + C_2H_2$, is estimated by titration with *N*/10-permanganate. The liberated acetylene does not introduce any complication. Test analyses with pure and diluted acetylene show the method to be accurate.

H. W.

Estimation of Chloroform and other Volatile Substances. A. SCHLICHT and WALTER AUSTEN (*Zeitsch. öffentl. Chem.*, 1920, **26**, 55—57).—To estimate chloroform in admixture with alcohol, 5 c.c. of the mixture are diluted with water to 200 c.c. and shaken with 60 c.c. of ether; after the ethereal layer has separated, its specific gravity is determined. An increase of 0·0001 in the specific gravity corresponds with 0·1786 gram of chloroform in 100 c.c. of the original mixture. W. P. S.

Thermal Analysis of the Products of Nitration of Naphthalene. P. PASCAL (*Bull. Soc. chim.*, 1920, [iv], **27**, 388—408).—A study of the melting-point curves of the binary mixtures, naphthalene-α-nitronaphthalene; 1:5-dinitronaphthalene-1:8-dinitronaphthalene; α-nitronaphthalene-1:5-dinitronaphthalene; α-nitronaphthalene-1:8-dinitronaphthalene; 1:5-dinitro-

ıaphthalene-1 : 3 : 5-trinitronaphthalene; 1 : 8-dinitronaphthalene- : 3 : 5-trinitronaphthalene; 1 : 5-dinitronaphthalene-1 : 3 : 8-trinitroıaphthalene; 1 : 8-dinitronaphthalene-1 : 3 : 8-trinitronaphthalene; : 3 : 8- and 1 : 2 : 5-trinitronaphthalenes; 1 : 3 : 5- and 1 : 2 : 5-trinitroıaphthalenes; 1 : 3 : 5- and 1 : 3 : 8-trinitronaphthalenes; 1 : 4 : 5- and : 3 : 8-trinitronaphthalenes; 1 : 4 : 5- and 1 : 2 : 5-trinitronaphthalnes; and of the ternary mixtures, nitronaphthalene and the two linitronaphthalenes; the two dinitronaphthalenes and each of the rinitronaphthalenes in turn; 1 : 3 : 5-, 1 : 3 : 8-, and 1 : 2 : 5-trinitroıaphthalenes. The application of these results to the analysis of ndustrial products of nitration of naphthalene is discussed.

W. G.

Estimation of Methyl Alcohol. A. Heiduschka and L. Volf (*Pharm. Zentr.-h.*, 1920, **61**, 361—366).—The methyl alcohol s heated at 100° for an hour in a closed vessel with sulphuric acid nd an excess of potassium dichromate; the quantity of carbon ioxide formed is then estimated gravimetrically by absorption in otassium hydroxide solution. The excess of dichromate is stimated volumetrically, and the quantity of methyl alcohol resent is calculated from the weight of carbon dioxide formed or rom the amount of oxygen required for the oxidation. The ethod may be applied to a mixture of methyl and ethyl alcohols, n allowance being made for the fact that 0·8% of the ethyl alcohol s also oxidised to carbon dioxide. [See, further, *J. Soc. Chem. nd.*, 1920, 558a.]

W. P. S.

Estimation of Ethylene Glycol. Bernhard Müller (*Chem. Zeit.*, 1920, **44**, 513—515).—Ethylene glycol, now used as subtitute for glycerol in Germany, may be estimated by the ichromate or acetin methods used in glycerol analysis, but the cetin method cannot be used for dilute solutions of the glycol. Oxidation with chromic acid and sulphuric acid, and gravimetric stimation of the carbon dioxide produced, also yields trustworthy esults. Ethylene glycol does not appear to be oxidised completely o oxalic acid by permanganate in alkaline solution.

W. P. S.

Analysis of Powders and Explosives. Differentiation of Glyceryl Trinitrate and of Ethylene Dinitrate. M. D. Marqueyrol and E. Goutal (*Bull. Soc. chim.*, 1920, [iv], **27**, 443—448).—When exposed in a desiccator over sulphuric acid at 2° and at the ordinary pressure, glyceryl trinitrate does not lose n weight, whereas ethylene dinitrate loses steadily. When a nixture of the two is so exposed, the loss in weight is directly roportional to the percentage of the latter in the mixture.

In 10% solution, glyceryl trinitrate and ethylene dinitrate cause espectively a lowering of 2·13° and 3·06° in the freezing point f benzene. With mixtures, the lowering is proportional to the mounts of the two substances present.

Either of these methods may be used for estimating the amount

of ethylene dinitrate in a sample of glyceryl trinitrate, and neither is vitiated by the presence of commonly occurring impurities, such as vaselin, diphenylamine, etc. W. G.

Estimation of Glyceryl Nitrate. H. Droop Richmond (*Analyst*, 1920, **45**, 260—265).—A method for the analysis of commercial "nitroglycerin" solution consists in diluting 10 c.c. of the sample with 50 c.c. of water and titrating the acidity with $N/10$-barium hydroxide solution; 0·1 c.c. is deducted from the volume of the latter solution required, and the result is divided by 1·02. To estimate the glyceryl nitrate, 5 c.c. of a 10% solution plus 5 c.c. of 90% alcohol, or 10 c.c. of a 5% solution, are treated with 25 c.c. of $N/2$-alcoholic sodium hydroxide solution; 20 c.c. of a 1% solution require 10 c.c. of the alkali solution. After five minutes, phenolphthalein is added, and the excess of alkali titrated with $N/1$-acid. If more than 4 c.c. of acid is used, the estimation must be repeated, increasing the quantity of alcohol, as the amount of water introduced must not exceed 10% of the total volume. The volume of alkali solution absorbed is corrected for the acidity; each c.c. of $N/1$-sodium hydroxide solution corresponds with 0·05675 gram of nitroglycerol. If 2 c.c. of 100 vol. hydrogen peroxide are added before the alkali is introduced, the final alcoholic strength has much less influence on the titration. W. P. S.

Volumetric Estimation of ββ′-Dichloroethyl Sulphide. William Francis Hollely (T., 1920, **117**, 898—902).

The Analysis and Composition of "Cresylic Acid." J. J. Fox and M. F. Barker (*J. Soc. Chem. Ind.*, 1920, **39**, 169—172T).—The "cresylic acid" used consisted of the tar acids distilling up to 210° and then refractionated up to 203° or 204°, such a fraction usually containing less than 10% of phenol. If more phenol is present, its proportion should be brought below 10% by adding a suitable amount of *m*-cresol. It is shown that Raschig's nitration process (A., 1900, ii, 694) for the estimation of *m*-cresol is sufficiently accurate for technical purposes. The authors obtained the best results by a slightly modified procedure in the first stage of the process. Ten grams of the "cresylic acid" are heated with 15 c.c. of 98% sulphuric acid in a 1200 c.c. flask until the liquid is viscous at the room temperature. By rotation, the liquid is spread in a thin layer over the bottom of the flask and 100 c.c. of nitric acid (D 1·4) is added, and the flask replaced on the water-bath. Raschig's procedure is then followed.

The following bromination method will give accurate results. One gram of the dried "cresylic acid" is weighed into a tared flask fitted with a ground-in stopper carrying a tap-funnel and an exit tube with a stopcock. Excess of a 20% solution of bromine in carbon tetrachloride is added drop by drop, and the mixture left for several hours. It is then warmed at a temperature not

exceeding 50° to expel bromine, and finally the solvent is distilled off under reduced pressure. The products of bromination are then weighed. The percentage of *m*-cresol is given by the equation $\% m\text{-cresol} = (100W - 246{\cdot}3)/0{\cdot}731$, where W is the weight of bromo-derivative obtained from 1 gram of the mixed cresols.

A modification of the method of Ditz and Cedivoda (A., 1900, ii, 54), in which the amount of bromine absorbed during bromination is estimated volumetrically, was found to be very rapid and sufficiently accurate for general work.

By estimating the percentage of *m*-cresol by one of these methods, and the percentage of phenol by the method previously described (A., 1917, ii, 513), or that of Dawson and Mountford (T., 1918, **113**, 923), and determining the $D_{15.5}^{15.5}$ of the mixture of cresols, the percentage of *o*-cresol present is given by $0{\cdot}0128O = 100(G - 1{\cdot}0388) - 0{\cdot}0386P$, where O is the percentage of *o*-cresol, P that of phenol, and G the value of $D_{15.5}^{15.5}$. The percentage of *p*-cresol is then obtained by difference from 100.

Finally, the authors reply to the criticisms of Dawson and Mountford (*loc. cit*) of the curves given in their last paper (compare A., 1918, i, 427). W. G.

Titration of Sugars. N. Schoorl (*Zeitsch. Nahr. Genussm.*, 1920, **39**, 180—182).—In the method described by Rupp and Lehmann (A., 1909, ii, 442) and Schowalter (A., 1919, ii, 172), the prescribed quantities of solutions must be employed in order that the tables may indicate the correct amount of dextrose. When an aliquot portion of the copper solution is titrated, the result must be corrected to the total volume before reference is made to the tables. W. P. S.

Detection of Oxalic Acid and Lactic Acid and Differentiation from Tartaric Acid. Kurt Brauer (*Chem. Zeit.*, 1920, **44**, 494).—When heated with a mixture of concentrated sulphuric acid and resorcinol, oxalic acid yields a brilliant violet coloration, whilst tartaric acid and lactic acid give red colorations. Tartaric acid gives a yellow, oxalic acid a green, and lactic acid a red coloration when heated with dilute sulphuric acid (1:1) and resorcinol. The colorations obtained are less characteristic when the resorcinol is replaced by phloroglucinol, catechol, or quinol. W. P. S.

A Reaction of Benzoic Acid Based on its Diazotisation; Its Application to the Toxicological Detection of Atropine, Cocaine, and Stovaine. Marcel Guerbet (*Compt. rend.*, 1920, **171**, 40—41).—The following procedure gives a ready means of detecting as little as 0·0001 gram of benzoic acid, or of substances such as cocaine or stovaine which contain a benzoyl group, or of atropine which on oxidation yields benzoic acid. The small amount of material is placed on a watch-glass, three or four drops of nitric acid (D 1·49) are added, and the mixture evaporated to dryness

on a water-bath. The residue is taken up with one drop of a 10% solution of stannous chloride, and after two or three minutes' warming, the nitrobenzoic acids are reduced. The liquid is allowed to cool, and two drops of a 1% solution of sodium nitrite are added, and finally, three drops of a 1% solution of β-naphthol in ammonia, when a bright orange-red precipitate is obtained if benzoic acid or one of the alkaloids mentioned above was originally present. The test may be confirmed by dissolving the azo-compound in 1 c.c. of concentrated sulphuric acid and pouring the solution into water, an orange-yellow colour resulting.

For toxicological work, the test may be applied to the extracts of organs prepared by Stas's method. W. G.

Analysis of "Saccharin." OSKAR BEYER (*Chem. Zeit.*, 1920, **44**, 437—438).—To estimate *o*-benzoicsulphinide in commercial "saccharin," 1 gram of the sample is titrated with $N/10$-potassium hydroxide solution, using phenolphthalein as indicator; the percentage quantity (x) is then calculated from the formula

$$x = 2{\cdot}01329 \times c - 100/0{\cdot}09845,$$

where c is the number of c.c. of $N/10$-solution used. The difference between the result and 100 gives the amount of *p*-sulphaminobenzoic acid present, provided other impurities are absent.

W. P. S.

Estimation of Acetaldehyde in Paracetaldehyde. F. VON BRUCHHAUSEN (*Apoth. Zeit.*, 1919, **34**, 428—429).—A description of experiments in view to the adaptation of an iodometric method, similar to that employed by Romijn in the case of formaldehyde, for estimating acetaldehyde in paracetaldehyde, whereby only negative results were obtained. Richter's sulphite method is best suited to the problem in question. CHEMICAL ABSTRACTS.

Estimation of Phytin in Plant Extracts. AUGUST RIPPEL (*Biochem. Zeitsch.*, 1920, **103**, 163—172).—Phytin can be precipitated more or less quantitatively in the presence of inorganic phosphates by copper acetate in acetic acid solution. Favourable results can only be obtained with definite concentrations of copper acetate and acetic acid. An extract from barley yielded 63·3% of the phytin-P_2O_5 by precipitation with copper acetate in a 1% acetic acid. The same method accounted for 92·8% of the phytin in standard solutions of that substance. The phytin in an acetic acid extract from peas could not be precipitated by copper acetate at all. S. S. Z.

A New Microchemical Reaction of Cystine Applicable to its Detection in Urinary Calculi. G. DENIGÈS (*J. soc. pharm. Bordeaux*, 1920, **58**, 8—12).—After pointing out the disadvantages of the methods in use at present, the author describes the following modified Esbach method for the identification of cystine in urinary calculi. A small quantity (1 mg. or more) of

the powdered or finely shaved material is placed on a glass slide, moistened with a drop of concentrated hydrochloric acid (D at least 1·17 or 1·18) added at the outer edge by means of a pointed glass rod, and examined under the microscope without the use of a cover-glass. The groups of prismatic needles, which rapidly increase in number, are cystine hydrochloride, and can be distinguished even with low magnification. After a few minutes, a drop of water is stirred in. The crystals will be observed to dissolve. This is characteristic of cystine hydrochloride, and serves to distinguish it from uric acid, which is insoluble under these conditions. The solution is evaporated to dryness over a flame, the residue is cooled, covered with a slip, and a drop of water is added at the edge. The formation of hexagonal plates of cystine will be observed after a few seconds. Two photomicrographs are presented showing the crystalline forms described.

CHEMICAL ABSTRACTS.

Estimation of Urea by Means of the Carbon Dioxide Evolved by Urease. S. PARTOS (*Biochem. Zeitsch.*, 1920, **103**, 292—299).—An apparatus is described by means of which urea is estimated from the carbon dioxide evolved from it by urease. Estimations of urea in artificial preparations, as well as in urine, are described which show only an error of the order of about 1%.

S. S. Z.

Rapid Detection of Morphine in the Toxicological Analysis of Viscera. LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1918, **6**, 349—351).—By means of the following method morphine was detected in the viscera after ingestion by the subject of only 0·002 gram: 120 grams of viscera are mixed with magnesia to a compact paste, which is completely dehydrated on the water-bath. The powdered residue is boiled with acetone, and the filtered extract treated with 2—3 c.c. of water and a few drops of acetic acid. The liquid is again filtered and evaporated on the water-bath. The residue containing the morphine is purified by treatment with 5% acetic acid, filtration, and extraction with boiling chloroform after addition of excess of ammonia. W. R. S.

Reduction Potentials of Mixtures of Indigotin and Indigo-white, and of Mixtures of Methylene-blue and Methylene-white. W. MANSFIELD CLARK (*J. Washington Acad. Sci.*, 1920, **10**, 255—270).—Measurements were made at 30° of the reduction potential of indigotinsulphonic acid and of methylene-blue solutions during titration with titanium trichloride over a considerable range of P_H values, from 1·55 to 8·58. To obtain the required values of the hydrogen-ion concentration, "buffer" salts were used, consisting either of citrate or mixtures of this with other salts. It was found that the sharpness of the end-point depended on the P_H value of the solution. This accounts, perhaps, for the empirical observation of Knecht and Hibbert, that a sharp end-point in the titration of many dyes with titanium trichloride

can only be obtained in presence of such substances as tartrates. In the case of indigotinsulphonic acid, the reduction potential varied from +0·2076 at P_H=1·55 to −0·1609 at P_H=8·58, and with methylene-blue from +0·3811 to −0·05 over the same range.

E. H. R.

Goiffon's Colorimetric Method for the Estimation of Stercobilin. V. BORRIEN (*Compt. rend. Soc. Biol.*, 1920, **83**, 211—212: from *Chem. Zentr.*, 1920, ii, 723).—In Goiffon's method (this vol., ii, 399) a portion of the hydrobilirubin is carried down by the precipitate and remains on the filter. The accurate estimation of the substance is only possible when it has been isolated in the chemically pure condition, which has not been effected up to the present. For clinical purposes, methods such as that of Triboulet, which permit a rapid approximate estimation of the dye, are sufficiently accurate.

H. W.

Estimation of Albumin in Urine containing Pus. LUIS ESPINOSA TAMAYO (*Bol. Lab. Mun. Guayaquil*, 1920, **1**, 33).—One hundred c.c. of filtered urine are treated with 1 c.c. of strong ammonia, stirred, and left to settle for a short time; in the presence of pus a gelatinous precipitate is formed, which is filtered off. The filtrate is treated with 20 c.c. of sodium chloride solution and 30% trichloroacetic acid to acid reaction; after half an hour's heating on the water-bath the precipitate is collected on a tared filter, and the determination completed as in Scherer's method. The albumin is easily filtered off. W. R. S.

Van Deen's Reaction and Hydrocyanic Acid. LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1918, **6**, 508—512).—Experimental proof is given that hydrocyanic acid, contrary to Selmi's statement (*Accad. Sci. Bologna*, 1879), does not interfere with Van Deen's reaction; on the other hand, potassium cyanide prevents the production of the blue coloration given by the reagent (hydrogen peroxide and tincture of guaiacum resin) in presence of fresh blood. This is shown to be due to the alkalinity of ordinary cyanide, as a positive reaction is obtained after neutralisation of the free alkali with acetic acid. Selmi's negative results must be attributed to the alkalinity of the cyanide used.

W. R. S.

The Carbon Dioxide Content as a Basis for Distinguishing Heated from Unheated Milk. LUCIUS L. VAN SLYKE and RICHARD F. KEELER (*J. Biol. Chem.*, 1920, **42**, 41—45).—It appears that normal unheated milk seldom, if ever, has a vol. % of carbon dioxide lower than 3·5—3. Pasteurisation reduces this value to 2·5 or less. Therefore, it appears safe, in general, to assume that milk containing less than 2·5 or 3 vol. % of carbon dioxide has been heated to the temperature of pasteurisation.

J. C. D.

General and Physical Chemistry.

Arc and Spark Spectra and the Periodic System. INGO W. D. HACKH (*Astrophys. J.*, 1918, **48**, 241—255).—A survey of the relations among number and intensity of lines in the arc and spark spectra and the *E.M.F.* and valency of elements. It is shown that elements of high electro-potential give few lines, elements of weak electro-potential give many lines, and that elements with a low polar number (1—3) show very intense lines, whilst those with a high polar number (above 5) show lines of weak intensity. The spectrum is thus not the result of a number of homogeneous atoms, but the average result of different atoms or atom species. Thus the elements with strong *E.M.F.* have few species of atoms, the electrons being arranged in a few definite positions, whilst elements of weak *E.M.F.* have many species, the electrons being arranged in a variety of systems. The paper contains also a spiral arrangement of the periodic system from which the new periodic table is derived (A., 1918, ii, 306, 396). CHEMICAL ABSTRACTS.

Spectrum of Hydrogen Positive Rays. G. P. THOMSON (*Phil. Mag.*, 1920, [vi], **40**, 240—247).—The positive ray spectrum of hydrogen has been examined under varying conditions in the discharge tube, whereby the proportion of atoms and molecules was varied over a wide range. The experiments show that the Balmer series is produced when positively charged hydrogen atoms pass through hydrogen as positive rays. The second spectrum is produced when positively charged hydrogen molecules pass through hydrogen as positive rays. The failure of Stark and Wilson to find the Döppler effect for the second spectrum of hydrogen is probably to be explained by the absence of molecules in the positive rays used. In certain circumstances a great change can be made in the nature of the positive rays given by a discharge tube by subjecting it to a magnetic field. J. F. S.

Krypton and Xenon. J. N. COLLIE (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 349—354).—A number of hitherto unmeasured lines have been observed in the spectra of xenon and krypton. The lines are observed with a fairly strong discharge, but still more are visible when a Leyden jar is placed in the circuit. It was found impossible to photograph the lines, which were therefore directly measured. In the case of xenon, 44 lines are recorded between λλ 7121 and 6036, and with krypton 35 lines between λλ 6768 and 5718 are measured. The lines are all of low intensity, but in the case of one experiment with xenon with a jar discharge the following brilliant lines were

seen: λλ 6880 (5), 6730 (5), 6669 (5), 6470 (7), 6318 (8), 6179 (8). It was observed that after passing a heavy current for some hours the xenon entirely disappeared and the tube became vacuous. This occurred with krypton and hydrogen, but with the difference that in the latter cases the gas was regained when the metal splashes were heated, whilst with xenon no gas could be recovered on heating the tube, electrodes, or splashes. The disappearance of the xenon occurs most readily with platinum electrodes, and aluminium and copper come next. No gas is evolved when the splashes are dissolved in acid or alkali, consequently there is no formation of a compound corresponding with a hydride, unless this, on treatment with alkali, forms an alkali xenate. J. F. S.

Revision of the Series in the Spectrum of Barium. F. A. Saunders (*Astrophys. J.*, 1920, **51**, 23—36).—A study of photographs taken by A. S. King of vacuum furnace spectra leads to the revision and extension of the known spectrum of barium.

Chemical Abstracts.

Character of the Absorption Spectra Produced by the Electric Furnace. II. The Zeeman Effect for Electric Furnace Spectra. III. Electric Furnace Spectra of Cobalt, Nickel, Barium, Strontium, and Calcium in the Region of Greater Wave-length. Arthur S. King (*Astrophys. J.*, 1920, **51**, 13—22, 107—120, 179—186).—I. By placing a plug of graphite in the middle of a vacuum tube furnace a continuous spectrum depending on the temperature was produced with which the pure absorption spectra of barium, calcium, cobalt, iron, and titanium were studied. Those lines which are most intense in emission spectra were not always the strongest in absorption spectra. The absorption at each temperature stage corresponded with the emission spectrum several hundred degrees lower. By placing the plug beyond the middle of the furnace mixed spectra were obtained which should help to explain stellar spectra containing both bright and dark lines. II. The Zeeman effect noted in spark spectra has been closely checked by a study of the vacuum furnace emission and absorption spectra of iron in a magnetic field. III. The infra-red spectra for cobalt, nickel, barium, strontium, and calcium are tabulated. The lines that appear in the arc spectra above a certain minimum intensity usually appear in the furnace spectra, but not always in the same relative strength. The rules that hold for the visible spectrum as to change in intensity of the lines with temperature change hold for the infra-red.

Chemical Abstracts.

Absorption Spectra of the Nitric Esters of Glycerol. Elliot Quincy Adams (*J. Amer. Chem. Soc.*, 1920, **42**, 1321—1327).—A theoretical consideration of the work of Hepworth (T., 1919, **115**, 840). It is shown that in plotting absorption spectra the use of the logarithm of the specific or molecular extinction-coefficient should be avoided, since it tends to obscure the rela-

tionship between absorption and constitution. The designations α and β- applied by Will (A., 1908, i, 384) to the two mononitrates derived from glycerol should be interchanged. It is possible that the "glycidnitrat" described by Nef (A., 1905, i, 3) is glyceryl orthonitrate. The absorption spectra of the nitric esters of glycerol as given by Hepworth (*loc. cit.*) can be completely accounted for on the assumption that each nitrate radicle has an absorptive effect dependent on its location in the molecule, but independent of the presence or absence of other nitrate radicles. The absorptive effect of the nitrate radicle is about 1·5 times as great when it replaces the β-hydroxyl of glycerol as when it replaces an α-hydroxyl group

J. F. S.

Dissociation of Iodine Vapour and its Fluorescence. St. Landau and Ed. Stenz (*Phil. Mag.*, 1920, [vi], **40**, 189—197).—The fluorescence of iodine vapour at low pressure has been examined with the object of ascertaining the effect of temperature and dissociation on it. It is shown that raising the temperature does not produce as great an effect on the fluorescence of iodine vapour as has hitherto been thought. Fluorescence has been observed at temperatures above 800°. Dissociation destroys both the fluorescence and the resonance spectra. Thus the complicated vibrating system, corresponding with thousands of absorption lines in the visible part of the spectrum, is not inherent in the atom, but in the molecule. The structure of the atom should therefore be relatively simple. This idea is perfectly in accord with other facts obtained from a study of the fluorescence of vapours. It appears nearly certain that the absorption lines, which are so characteristic for diatomic iodine and so sensitive to the action of monochromatic light, do not belong to the absorption spectrum of monatomic iodine. J. F. S.

Radiating Potentials of Nitrogen. H. D. Smyth (*Physical Rev.*, 1919, **14**, 409—426).—The author has derived an equation for making accurate corrections for the distribution of velocities among the impacting electrons which are used to obtain radiating potentials. This correction applied to the results obtained on the radiating potentials of nitrogen has given the following values: at $8·29 \pm 0·04$ volts a strong resonance, at 7·3 volts a doubtful resonance, at $6·29 \pm 0·06$ volts strong resonance at low pressures. The first value is probably connected to the Lyman doublet wave-lengths 1492·8 and 1498·8 Å.U. by the relationship $P.D. \times q = h\nu$. The author finds some difficulty in identifying the other potentials accurately with nitrogen lines. On an assumption identifying the last resonance potential (that is, at 6·29 volts) with a line of wave-length from 2000 to 3000 Å.U. coming from neutral atoms, it is estimated that the upper limit for the heat of dissociation of the nitrogen mol. is 190,000 cals. per gram-mol. Chemical Abstracts.

The Relative Activity of Radium and the Uranium with which it is in Radioactive Equilibrium. J. H. L. Johnstone and B. B. Boltwood (*Phil. Mag.*, 1920, [vi], **40**, 50—67).—A re-

determination of the ratio of the α-activity of uranium, in equilibrium with its disintegration products, to that of the uranium (UI and UII) alone gave 4·73, in good agreement with Boltwood's first value, 4·69. The comparison was made with very thin films of the material, and in the case of the mineral, which was a selected specimen of uraninite from Spruce Pine containing 73% of uranium, the result was corrected for loss of emanation, and for thorium (1·9% ThO_2) present. The ratio of the α-activity of the radium itself to the uranium in the mineral was found to be 0·488, as compared with the first value, 0·45, and is far lower than the value, 0·57, deduced from the two-thirds power of the range of the respective α-rays emitted, if the transformations involved were simple and direct. However, the first ratio, 4·73, is in excellent agreement with the value so calculated on the experimental datum that the branch actinium series contributes 0·28 to it. The last corresponds with a proportion of 8% of the uranium forming actinium and 92% radium. Now the two schemes proposed by Soddy and Cranston (A., 1918, ii, 211) for the origin of the actinium series require a ratio 0·55 and 0·53, according as the branch occurs at UI or UII, instead of the experimental value 0·488 already cited, if the actinium branch is 8%. Or, for the experimental value to be accounted for, an actinium branch of 26 or 14% respectively is required. Various possibilities are discussed without clearing up the discrepancy (compare Hahn and Meitner, this vol., ii, 147). F. S.

Resonance and Ionisation Potentials for Electrons in the Monatomic Gases, Argon, Neon and Helium. H. C. Rentschler (*Physical Rev.*, 1920, **14**, 503—515).—With special precautions for eliminating impurities from the electrodes the author, using two methods (that of Tate and one similar to Lenards' first method), determined the resonance and ionisation potentials for argon, neon, and helium. He found ionisation potentials for helium to be about 26 volts, for neon about 19·5 volts, and for argon about 17 volts. Resonance potentials were only observed for the case of argon at about 12 volts. The accuracy of the values found is not great, as no correction was made for the initial velocities of the electrons. Chemical Abstracts.

Ionisation and Resonance Potentials for Electrons in Vapours of Lead and Calcium. F. L. Mohler, Paul D. Foote, and H. F. Stimson (*Phil. Mag.*, 1920, [vi], **40**, 73—79).—The metal is boiled at low pressure in a tube containing a Wehnelt cathode surrounded by a cylindrical grid and a plate, a variable potential to accelerate the electrons being applied between the cathode and the grid, and a small retarding field between the grid and the plate. A sudden increase in the electron current leaving the cathode as the accelerating potential is increased shows when the ionisation point is reached. The "partial current," grid to plate, decreases when the electrons near the grid lose their velocity by inelastic collisions, as is the case when the velocity

exceeds the resonance potential. For lead, a mean value of 1·26 volts for the resonance potential and 7·93 volts for the ionisation potential was obtained, which, by the quantum relation, correspond with wave-lengths 9800 Å. and 1550 Å. For calcium, two resonance potentials, at 1·90 and 2·85 volts, were found, the first being more prominent, and an ionisation potential of 6·01 volts. These are associated with the wave-lengths 6572·78 Å. (1·877 volts), 4226·73 Å. (2·918 volts), and 2027·56 Å. (6·081 volts). F. S.

Electrical Conductivity of Mixtures of Salts in the Fused and Solid States. C. SANDONNINI (*Gazzetta*, 1920, **50**, i, 289—321). —Using the arrangement devised by Kohlrausch, the author has measured the electrical conductivities of various binary mixtures of salts belonging to each of the three groups: (1) mixtures the components of which are miscible in the fused, and, maybe, also in the solid, state, but do not combine; (2) mixtures forming compounds decomposed on fusion; (3) mixtures forming one or more compounds stable in the fused condition. The systems examined were: (1) $PbCl_2$–$PbBr_2$, AgCl–AgBr, $NaNO_3$–KNO_3, NaCl–KCl. (2) AgCl–TlCl, NaCl–$CaCl_2$. (3) $AgNO_3$–$TlNO_3$, KCl–$CaCl_2$, TlCl–$CdCl_2$, KCl–$CdCl_2$.

The conductivities of the fused mixtures are in all cases found to be lower than the values calculated from the law of mixtures. With certain pairs, the conductivity isotherms exhibit minima, this occurring principally when the components combine. Such minima do not, however, correspond always with the compounds formed, and with the system NaCl–$CaCl_2$ a minimum conductivity occurs at a temperature at which, according to thermal analysis, the compound formed by the two salts is completely dissociated, and at a composition far different from that of the compound.

From the values of the specific conductivity alone, certain deductions cannot be drawn, since variations of volume taking place during reciprocal dissolution of the two salts result in variation of the ionic concentrations. The author has therefore determined the densities of the following typical fused mixtures of salts: $NaNO_3$–KNO_3, NaCl–KCl, NaCl–$CaCl_2$, and KCl–$CaCl_2$. In these cases, the variation in specific gravity occurring during mixing is very small, even when the presence of complex molecules in the fused mass may be assumed.

The equivalent conductivities for these mixtures have been calculated, the changes in density being taken into account. With those pairs of salts for which compounds exist in the fused mass, the differences between the observed and calculated conductivities are certainly the more marked, but the isotherms in general exhibit no singular points corresponding with the compositions of the compounds, although with KCl–$CaCl_2$ this is approximately the case.

Conductivity measurements have also been made on the following solid mixtures: $PbCl_2$–$PbBr_2$, AgCl–AgBr, and AgCl–TlCl. The results obtained show that, when the solidified salt mixtures

consist of solid solutions which may be regarded as perfectly homogeneous, the phenomena encountered with mixtures of aqueous solutions or of fused salts having a common ion are repeated, the electrical conductivity being less than the calculated value. For the system TlCl–AgCl, the conductivity curve exhibits a maximum coincident with the eutectic concentration (compare Benrath, A., 1909, ii, 12; Benrath and Wainoff, A., 1911, ii, 847), whereas the formation of solid solutions being excluded in this system, the presence in the mass of a double salt should produce a diminution, and not an increase, in the conductivity. The probable cause of this increase lies in a diminution of the internal friction, which, for a given isotherm, will be the lower as the temperature approaches more nearly the melting point. T. H. P.

The Rectifying Contact Galena-metal. Artificial Sensitisation and Different Remarks. C. Florisson (*Compt. rend.*, 1920, **171**, 106—108).—Artificial sensitisation produces the rectification *B* in specimens of galena having a slight original rectification *A*. Various methods of promoting this change were examined. The metal used for the contact is platinum. Heating in an atmosphere of nitrogen has, as a rule, no effect, although in a few cases the rectification *B* was produced. The action of air at high temperature not only did not produce the rectification *B*, but tended to destroy it in specimens where it was apparent. The action of pure dry sulphur dioxide was very irregular, but sulphur vapour in a current of nitrogen almost invariably caused marked sensitisation. Selenium was similar, but much less marked in its action. In all these cases where sensitisation occurred, a very thin, superficial layer was apparently produced, which probably contained more sulphur than lead sulphide, the sulphur being present either in combination or in solid solution. The presence of this layer in naturally occurring sensitive galenas is discussed. W. G.

Anode Corrosion of Lead in Sodium Hydroxide Solutions. O. W. Brown, C. O. Henke, and L. T. Smith (*J. Physical Chem.*, 1920, **24**, 367—378).—The corrosion of lead anodes during the electrolysis of solutions of sodium hydroxide of various concentrations has been examined at 20°, 60°, and 75°, using current strengths of various values and an *E.M.F.* of about 3 volts. It is shown that the amount of corrosion increases rapidly with increasing temperature; thus, using a solution of 152 grams of sodium hydroxide per litre, the amount of corrosion is 4·5% of the theoretical at 20°, 98·3% at 60°, and theoretical at 75°. At all temperatures, the corrosion increases with increasing concentration of sodium hydroxide to a maximum, which is reached at 152 grams per litre, and then falls, with a further increase in concentration. Thus at 60° the following fractions of the theoretical amount of corrosion are observed with the given concentrations: 35 grams/litre, 5·7%; 71 grams/litre, 49·3%; 110 grams/litre, 96·4%; 152 grams/litre, 98·3%; 192 grams/litre, 58·5%; 220 grams/litre

31·5%; and 304 grams/litre, 37·7%. The current efficiency increases rapidly with increase of temperature; this is especially marked where the concentration is 152 grams/litre and the current density 4 amperes/sq. dcm. The discharge potentials and the total polarisation have been determined for various current densities at 75° for a solution containing 152 grams/litre. It is found that there is 100% corrosion when the bath tension is low (0·2—0·3 volt), and a low corrosion when the voltage is high, 3·2. The total polarisation increases from −0·179 volt with a current density 1·56 amperes/sq. dcm. to −2·484 volts with 4·22 amperes/sq. dcm. When the anode is corroding properly, the discharge potential is about 0·2 volt, but when it ceases corroding, the discharge potential rises to −1·317 volts. J. F. S.

Ballo-electricity, Molecular Forces, and Electrical Forces. J. Traube (*Ann. Physik*, 1920, [iv], **62**, 165—172. Compare Christiansen, A., 1919, ii, 385).—A theoretical paper in which the author considers the results of Christiansen's work. It is shown that the ballo-electric charge of solutions runs parallel with the surface tension; aballistic substances are shown to be without effect on the surface tension, whilst cataballistic and anaballistic substances have considerable influence on the surface tension of the solvent. In the case of homologous series of organic acids and bases, it is shown that there is a continuous increase in the surface tension and the ballo-electric charge of the solutions with increasing molecular weight. It is shown that the molecular forces and the forces of cohesion, like the chemical affinity, are electrical in origin. J. F. S.

Mobility of the Electrolytic Ions. M. Born (*Zeitsch. Physik.*, 1920, **1**, 221—249).—A mathematical paper. An expression is deduced for calculating the radii of the ions. The radii of the alkali metal ions and the halogen ions have been calculated to be somewhat less than 10^{-8} cm. It is further shown that the magnitude of the radius increases with the atomic number of the atom from which the ion is formed, and, for the same atomic number, that the radius increases with the magnitude of the charge carried by the ion. Chemical Abstracts.

Magnetic Susceptibilities of Quartz, Tellurium, and some Holmium Compounds. Gillis Wistrand (*Diss. Uppsala*, 1916, 56 pages).—Samples to be tested were fastened to a glass plate which could be moved in and out of a magnetic field produced by two Ruhmkorff coils. The effect of forces acting on the samples was determined by weighing. The sample was hung by a fine copper wire, 1 metre long, to the underside of the pan of a precision balance, the sample hanging free between the electromagnetic poles. Samples investigated were two clear quartz cylinders about 10 cm. long, and practically free from iron, a bar of tellurium about 4 cm. long, commercial samples of ferric hydroxide, manganese dioxide and manganese sulphide, and ferric oxide, made by

heating ferric hydroxide; holmium oxide was tested in three fractions, because of the varying presence of other rare metals; the nitrate and chloride were also investigated. Similar determinations for comparison were made on water in a thin glass tube. The author found the specific magnetic susceptibility (x_s) of water corrected for air to be $-0{\cdot}7260 \times 10^{-6}$, for quartz in vacuum $-1{\cdot}070 \times 10^{-6}$, for tellurium $-1{\cdot}70 \times 10^{-6}$, for ferric hydroxide $123{\cdot}8 \times 10^{-6}$, for ferric oxide $60{\cdot}7 \times 10^{-6}$, for manganese dioxide $37{\cdot}3 \times 10^{-6}$, and $64{\cdot}80 \times 10^{-6}$ for manganese sulphide. $x_s = +132{\cdot}6 \times 10^{-6}$ and $+172{\cdot}0 \times 10^{-6}$ for holmium nitrate and chloride respectively, which gave 51·4 as the value of the "magneton" number of holmium. $x_s = +243 \times 10^{-6}$ was the average of the three fractions of holmium oxide, the fractions giving 51·4, 50·7, and 51·5, respectively, as the magneton numbers.

CHEMICAL ABSTRACTS.

Calorimetric Method for Standardising Thermometers by Electrical Energy. THEODORE W. RICHARDS and SETSURO TAMARU (*J. Amer. Chem. Soc.*, 1920, **42**, 1374—1377).—Thermometers may be standardised by immersing them in a calorimeter containing a known amount of water at a measured temperature, and adding measured amounts of heat by allowing a known electric current of suitable voltage through a definite resistance to enter the liquid, thus adding a measured quantity of electrical energy. The rise of temperature can then be calculated and compared with the temperature registered by the thermometer. This method is capable of giving results of the greatest accuracy. As an example of the method, a measured quantity of electrical energy was added nine times in succession to a calorimeter (adiabatic) containing a Beckmann thermometer. The readings were 2·0505°, 2·5555°, 3·0510°, 3·5475°, 4·0440°, 4·5375°, 5·0320°, 5·5225°, and 6·0080°. Allowing for the difference of specific heat of water, the error in the thermometer is found to be +0·0102° between 2·55 and 3·05, and so on.

J. F. S.

The Expansion of Saturated Vapours. G. BRUHAT (*Compt. rend.*, 1920, **171**, 162—164).—A mathematical discussion of the subject.

W. G.

Specific Heat of Saturated Vapours and Entropy-temperature Diagrams of Fluids. ALFRED W. PORTER (*Phil. Mag.*, 1920, [vi], **40**, 211—212).—The author discusses some points in a paper under the above title by Ewing (this vol., ii, 412). It is shown the specific heat of the saturated vapour in the case of sulphur dioxide can be positive, and that the inversion temperatures are 97·5° and 114°. The entropy of a liquid is not $\int_0^t C_p \, . \, dT/T$, where C_p is the specific heat at constant pressure, even with the proviso that the value of C_p must be taken at saturation. The value of C_p must be replaced by K_w, the specific heat of saturated liquid. The difference between C_p and K_w is negligible at temperatures suffi-

ciently remote from the critical temperature, but it tends towards $+$ infinity as the critical temperature is approached. The relation between the two quantities is $K_w = C_p - T(\delta v/\delta T)_p \cdot dp/dT$, or, in terms of the specific heat at constant volume (C_v), it may be expressed $K_w = C_v - T(\delta p/\delta T)_v/(\delta p/\delta T)_T \cdot ds/dT$, where s is the specific volume of the liquid at saturation. The values of K_w for sulphur dioxide are given for the range $-20°$ to $155·5°$, and it is shown that K_w is not a linear function of the temperature even in regions remote from the critical region. J. F. S.

Method of Suppressing the Correction of Temperature in the Determination of Melting-points. MAURICE FRANÇOIS (*Bull. Soc. chim.*, 1920, [iv], **27**, 528—536).—The apparatus used is a long-necked flask having two side-tubes, one near the bulb and the other being the continuation of the neck of the flask. These two side-tubes are joined by a vertical tube, which is continued upwards and expanded into a bulb. The flask and vertical tube are filled with oil to just above where the elongated neck joins the vertical tube. The material under examination is placed at the closed end of a long capillary tube, which is then bent back on itself. This tube is attached to the bulb of a thermometer, which is then placed in the vertical tube connected with the flask, the scale of the thermometer thus being in the oil. By this means a correction for exposed stem is avoided. A simple arrangement of mirrors is described by means of which it is possible to read the thermometer and observe the material in the melting-point tube simultaneously through one telescope. W. G.

Estimation of Impurities by means of the Melting-point Curve. WALTER P. WHITE (*J. Physical Chem.*, 1920, **24**, 393—416). —A theoretical discussion, accompanied by practical examples of methods of determining melting points and the estimation of impurities from the melting-point curves. It is shown that freezing points are more accurately determined by immersing the thermometer in the substance than by the capillary tube method. If, in addition, the form of the freezing-point curve is observed, an indication of the amount of impurity present is obtained, which is independent of all previous knowledge or uncertainty as to the melting point of the pure substance and even of the absolute accuracy of the thermometer. If the determinations are a control of a purification process, there is also a saving of time and the avoidance of certain chances of error. Smallness of dimensions of the melting tube diminishes local temperature differences, and is very often a superior substitute of the stirring rod. It also economises both time and material. A small thermocouple or cell of several couples is very useful with small test samples. The complications, usually almost negligible, arising from specific heat, uneven temperature, and other causes are considered, and suitable experimental arrangements are suggested for removing them. J. F. S.

Reduced Transition and Freezing Points. J. NARBUT (*Physikal Zeitsch.*, 1920, **21**, 341—349).—A mathematical paper, in which a number of relationships between the transition temperature and melting points of substances respectively are deduced. It is shown that at similar reduced temperatures the ratio between the transition affinity or the fusion affinity and the heat of transition or the heat of fusion of substances at the transition temperature or the melting point, Θ, respectively is the same for all substances $A'_{T'}/U'_{\Theta} = A''_{T'}/U''_{\Theta}$. The ratio between the transition or fusion affinity and the transition or fusion temperature, Θ, for similar reduced temperatures is the same for all substances with the same entropy value, S_{Θ}. $A'_{T'}/\Theta' = A''_{T'}/\Theta''$. A similar relationship exists between the heat of transition or the heat of fusion and the corresponding temperature, $U'_{T}/\Theta' = U''_{T'}/\Theta''$. The heat of fusion or transition may be calculated from the vapour pressure of the supercooled liquid or solid substance, or that of the labile and stable modifications by means of the formula

$$U_{\Theta} = 2R\Theta\phi/(1-\phi^2) \,.\, \log_e p_2/p_1.$$

The vapour-pressure curves of a supercooled liquid may be deduced if the vapour-pressure curve of the solid is known or vice versa. The ratio of the vapour pressure of the supercooled liquid and solid or the labile and stable modifications of a substance at the same reduced temperature is the same for all substances, $p_2'/p_1' = p_2''/p_1''$. At similar reduced temperatures the relationship $\sqrt[s'\Theta']{p_2'/p_1'} = \sqrt[s''\Theta'']{p_2''/p_1''}$ holds for supercooled and solid substances or for the labile and stable modifications of a substance. The formulæ have been applied to the known data for benzene, water, and the halogen derivatives of benzene, and shown to hold very exactly. J. F. S.

Practical Method of Determining the Boiling Point, with Small Amounts of Substance. VICTOR ABREGUINE (*Soc. Chim. Argent.*, **3**, 133 [reprint]).—The apparatus consists essentially of a small test-tube, 80—85 mm. long and 9 mm. in diameter, having a loose inner tube open at one end and a bulb at the other end, being about 5 mm. in diameter and 52—54 mm. long. This inner tube is first filled with mercury to within 1 mm. of the top, and the liquid under examination is added. This tube is inverted into mercury in the test-tube, which is then filled with glass beads and closed with a metal cap. The whole apparatus is placed against the bulb of a thermometer and slowly heated in a bath of a suitable liquid. The temperature is read on the thermometer, when the mercury is at the same level in the test-tube and the inner tube. Certain corrections, all very small in amount, must be made for the vapour pressure of mercury and for the error produced by excess of liquid in the inner tube. Formulæ are given for calculating these. The method is only applicable for liquids having boiling points below 210°. W. G.

Spontaneous Evaporation. HARRY B. WEISER and EVERETT E. PORTER (*J. Physical Chem.*, 1920, **24**, 333—341).—The present paper records the results of a repetition of some of Babington's

experiments (*Proc. Roy. Soc.*, 1859, **10**, 132) on the spontaneous evaporation of solutions. In this paper it was stated that solutions of potassium ferrocyanide, potassium tartrate, copper sulphate, and potassium chlorate evaporated more rapidly than pure water under the same conditions. A number of experiments have been made with solutions of these substances of various concentrations, and the rate of evaporation determined. It is shown that to obtain reproducible results the containers must be scrupulously clean, and that they must be slowly rotated on a revolving platform. Crystallisation must all take place on the base of the dish, and there must be no creeping. It is shown that in all cases, even with saturated solutions, the evaporation is slower than with pure water. Taking the precautions mentioned, this method may be used for obtaining a fairly accurate measurement of the relative lowering of the vapour pressure of various substances. A number of comparison experiments on the evaporation of solutions of sulphuric acid and chromium trioxide indicate that the latter exists in dilute solution chiefly as dichromic acid, as was pointed out by Ostwald from other considerations. J. F. S.

Vapour Pressures of certain Substances: Chloropicrin, Cyanogen Bromide, Methyldichloroarsine, Phenyldichloroarsine, Diphenylchloroarsine, and Arsenic Trichloride. G. P. BAXTER, F. K. BEZZENBERGER, and C. H. WILSON (*J. Amer. Chem. Soc.*, 1920, **42**, 1386—1393).—The vapour pressures of the substances named in the title have been determined at a series of temperatures by the air current method, except in the case of arsenic trichloride at higher temperatures, where the static method was employed. The vapour pressure in all the cases can be expressed by a formula of the type $\log p = A + B/(273+t)$; values of A and B have been deduced in each case. The following equations and values actually measured have been obtained: chloropicrin, $\log p = 8{\cdot}2424 - 2045{\cdot}1/273+t$; $-20°$, 1·50 mm.; $-19°$, 1·70 mm.; $-18°$, 1·90 mm.; 0°, 5·71 mm.; 10°, 10·37 mm.; 15°, 13·82 mm.; 20°, 18·31 mm.; 25°, 23·81 mm.; 30°, 31·10 mm.; 35°, 40·14 mm.; cyanogen bromide, $\log p = 10{\cdot}3282 - 2457{\cdot}5/273+t$; $-17{\cdot}3°$, 5·9 mm.; $-15{\cdot}5°$, 6·3 mm.; 0°, 21·2 mm.; 15°, 63·3 mm.; 25°, 119·5 mm.; 35°, 223·5 mm.; methyldichloroarsine, $\log p = 8{\cdot}6944 - 2281{\cdot}7/273+t$; $-17°$, 0·60 mm.; $-16{\cdot}8°$, 0·61 mm.; $-15°$, 0·71 mm.; 0°, 2·17 mm.; 15°, 5·91 mm.; 25°, 10·90 mm.; 35°, 19·33 mm.; phenyldichloroarsine, $\log p = 9{\cdot}150 - 3164/273+t$; 0°, 0·004 mm.; 15°, 0·014 mm.; 25°, 0·035 mm.; 35°, 0·076 mm.; 45°, 0·159 mm.; diphenylchloroarsine, $\log p = 7{\cdot}8930 - 3288/273+t$; 25°, 0·0003 mm.; 45°, 0·0039 mm.; 55°, 0·0065 mm.; 65°, 0·0148 mm.; 75°, 0·0282 mm.; arsenic trichloride, $\log p = 7{\cdot}5183 - 1720/241{\cdot}2+t$; 0°, 2·44 mm.; 25°, 11·65 mm.; 35°, 19·53 mm.; 50°, 40·90 mm.; 60°, 64 mm.; 70°, 97 mm.; 80°, 145 mm.; 90°, 211 mm.; 100°, 301 mm. The following heats of vaporisation have been calculated by means of the Clausius-Clapeyron formula,

$$L = T\,.\,dp/dt(V_{gas} - V_{liq.-solid}).$$

Chloropicrin, 35°, 6·77; 0°, 7·10; cyanogen bromide, 35°, 8·08; 0°, 8·60; arsenic trichloride, 100°, 6·86; 50°, 7·29; 0°, 7·42. An accuracy of a few per cent is claimed for the numerical values.

J. F. S.

Determination of the Last of the Three Functions which Define the Equation of State of Ethyl Ether. E. ARIÈS (*Compt. rend.*, 1920, **171**, 154—156).—The values of the functions x and Φ, which define the equation of state of ethyl ether (compare this vol., i, 418), have been determined, and it is necessary only to determine the values of a for the equations $v_1 = RT_c x(a + y_1)/8P_c\Phi$ and $v_2 = RT_c x(a + y_2)/8P_c\Phi$. Using the values obtained experimentally by Young for the liquid state, it is possible to calculate the numerical values of a for each 10° and to find an expression which represents this function:

$$a = a_c + (1 - \tau)^2/10^{\Theta},$$

where $\Theta = (A + B\tau + C\tau^2 + D\tau^3)/0{\cdot}0073688$ and the value of a_c is given by $v_c = RT_c(a_c + 2)/8P_c$ which gives $a_c = 0{\cdot}09809$.

The results calculated from these formulæ are in close agreement with those found experimentally by Young. W. G.

Equation of State. M. P. APPLEBEY and D. L. CHAPMAN (*Phil. Mag.*, 1920, [vi], **40**, 197—200).—The mean kinetic energy of translation of a molecule can no longer be assumed to be proportional to the temperature, and consequently the dynamical definition of temperature must be abandoned. From this point of view the authors deduce a new equation of state. They start with the assumption "that in a closed space which contains a large number of similar molecules the ratio of the number of molecules per unit volume whose potential energy is A to the number of molecules per unit volume whose potential energy is zero is given by the expression $e^{-A/kt}$, in which k is the gas constant for a single molecule and t the thermodynamic temperature." The final form of the equation deduced is $[Pb'/(e^{Pb'/kt} - 1)] + Pb'/2 = \frac{1}{3}mV^2/2$, in which m is the mass of a single molecule of the gas and b' the volume of fluid displaced by the molecule. J. F. S.

Equation of Condition. C. DIETERICI (*Ann. Physik*, 1920, [iv], **62**, 75—94).—A theoretical paper, in which the author considers the pressure isothermals obtained by Young (A., 1899, ii, 633) for *iso*pentane and by Amagat (A., 1893, ii, 152) for carbon dioxide. It is shown that the difference between the ideal saturation work, $A_{id} = RT \log_e v_2/v_1$, and the actual work, $A_s = p_s(v_2 - v_1)$, is given by the expression $(a - RTv_k)(S_1 - S_2)$, in which S_1 and S_2 are the saturation densities and a a constant which is determined by the critical data alone. J. F. S.

Correspondence of Substances in the Solid State. FÉLIX MICHAUD (*Compt. rend.*, 1920, **171**, 241—243).—The law of corresponding states has been generalised by making coincide certain

homologous points instead of the critical points (compare Curie, *Arch. Sci. phys. nat.*, 1891, **26**), and taking as specific units the co-ordinates of these points. There exists such a point in the solid region which is particularly useful. It has been shown that the specific heat, C, tends towards zero as the absolute temperature, T, approaches zero. Consequently, $C/T=0$ when $T=0$, and it also tends towards zero for $T=\infty$, and in consequence it must pass necessarily through a maximum, and it is this point, where the temperature is T_m, that is taken as a centre of correspondence. Thus the law of Dulong and Petit is only exact when the substances are taken in their corresponding states, as just defined, that is, at the absolute temperatures proportional to the temperatures T_m. It further results that the atomic entropies, at temperatures proportional to the temperatures T_m, are equal. These facts are demonstrated in the cases of aluminium, silver, copper, lead, and zinc. W. G.

Calorimetric Procedure for Determining the Heat of Slow Reactions. I. Analysis of Partially Concurrent Heat Effects. FREDERICK BARRY (*J. Amer. Chem. Soc.*, 1920, **42**, 1295—1308).—A theoretical paper in which the method of extrapolating, from a time–temperature change curve of two concurrent reactions, the temperature change of a single process is developed. In the case of the inversion of sucrose by acid, the heat changes are two: (1) heat of solution of the solid sucrose in the acid solution, and (2) heat of inversion. This case is considered as well as the cases where there is concurrent heat reaction in the same sense, that is, both exothermic or both endothermic, and concurrent heat reactions in opposite senses, as in the case of sucrose and dilute acid. Equations are developed whereby extrapolation of the desired heat change may be made from the experimental curves. J. F. S.

Thermochemistry of Hydrocarbons according to P. W. Zubov's Data. W. SWIETOSLAWSKI (*J. Amer. Chem. Soc.*, 1920, **42**, 1312—1321. Compare this vol., ii, 470).—A theoretical paper in which the values recalculated by the author from Zubov's data (*loc. cit.*) are critically examined. By analysis of the equations for the combustion of hydrocarbons, the terms $(y+w-2z)=Y$ and $(x+w-z-w)=X$ are obtained, which correspond respectively with the heats of combustion of the linkings C–C and C–H; y is the heat of formation of the atomic linking C–C, x that of C–H, $2w$ the heat of formation of the molecule O_2, $4z$ that of CO_2, and $2w$ that of H_2O. The terms X and Y are termed the thermochemical characteristics of the C–C and C–H linkings respectively. These characteristics have remarkably constant values in the case of *n*-hexane, *n*-octane, *n*-decane, *cyclo*hexane, and naphthalene. Hence, if the molecule of naphthalene contains the double bond C=C, the heat of formation of this double bond is exactly the same as that of two single bonds, C–C. The value of X and Y for

methane and ethane are exactly the same as in the cases mentioned above. The following values of the thermochemical characteristics X and Y and of the homologous difference Z are $X = -53{\cdot}72$ cal., $Y = -52{\cdot}25$ cal., $Z = 2X + Y = -157{\cdot}77$ cal. In spite of the proved constancy of X and Y in five saturated, one polymethylene, and one aromatic hydrocarbon, they are shown to vary in other hydrocarbons. It is definitely established that the heat of formation of the C–C linking increases with the increase of the number of carbon atoms in the polymethylene hydrocarbons, and that the heat of formation of the same linking is increased by the replacement of a hydrogen atom by a methyl or a *n*-propyl group. The increase in Y is not considerable. In the case of the polymethylene hydrocarbons, it varies between $-0{\cdot}5$ and $+0{\cdot}5$ in the series *cyclo*pentane, *cyclo*hexane, *cyclo*heptane. It varies within the limits $-0{\cdot}8$ and $+1{\cdot}7$ when one, two, or three methyl groups are introduced in the molecule of the polymethylene hydrocarbons. The analysis of the data on unsaturated hydrocarbons shows the important difference $2(y - y_2)$ between the heat of formation of two single linkings, C–C, and that of the double one, C=C. This difference, due to the change of constitution of the hydrocarbon examined, varies within the very large limits, $+8{\cdot}0$ cal. to $+1{\cdot}0$ cal. In special cases it is possible that $2(y - y_2)$ can be equal to zero, for example, in the case of naphthalene. J. F. S.

Static Friction. II. W. B. HARDY (*Phil. Mag.*, 1920, [vi], **40**, 201—210. Compare *ibid.*, 1919, [vi], **38**, 32).—The relationship between chemical constitution and the lubrication of bismuth has been examined at 11—14° by measuring the static friction between a burnished bismuth surface and bismuth slider, 70·5 grams weight and 25·5 mm. radius of curvature, lubricated by a large number of pure organic substances, which included thirteen alcohols, ten acids, two ketones, six esters, nine hydrocarbons, all of these of the aliphatic series, and forty-five cyclic compounds. It is shown that static friction is a function of the molecular weight of the lubricant, and in a simple series of chain compounds, such as fatty acids, alcohols, or paraffins, a good lubricant will be found if the series is taken high enough. It is by no means a simple function; the friction, for example, rises sharply in moving from chloroform to carbon tetrachloride, and from phenol to quinol and catechol. The influence of molecular weight is overshadowed by constitution. A linear relationship is found in the series benzene, naphthalene, anthracene, the paraffins, and ammonia–propylamine. In the aliphatic acids and alcohols, the linear relation to molecular weight is disturbed by the weighting of the chain at one end by the $-CO_2H$ and $-OH$ groups respectively. In a simple chemical series, lubrication and viscosity change in much the same way with molecular weight, but there is no fundamental relation between viscosity and lubrication. The curves for acids, alcohols, and paraffins show no break where, with increasing molecular weight, the lubricant becomes a solid at the temperature of observation,

as is shown by the pairs, benzene–naphthalene, menthone–menthol, thymol–carvacrol. The upward trend of the first part of the curve for the aliphatic alcohols is in agreement with the fact that methyl alcohol is abnormal in some of its physical properties. In their qualities as lubricants of bismuth, ring compounds are the converse of chain compounds; thus, the effect of a double bond is to decrease the lubricating value of the former and increase that of the latter. On the other hand, the presence of unsaturated atoms increases the lubricating qualities of chain compounds, whether it be the double-bonded oxygen of ketones or acids, or carbon of olefines and alcohols, but this rule is departed from in the case of acids when the chain becomes much elongated. When a ring and chain are joined, as in butylxylene, the product is a better lubricant than either constituent. When the atoms are disposed with complete symmetry about a carbon atom, the compound is a very bad lubricant, as is seen in the case of carbon tetrachloride and pentaerythritol, $C(CH_2 \cdot OH)_4$. In the ring compounds, the replacement of hydrogen decreases lubricating power in the case of N, :O, or $-CO_2H$, and increases it in the case of other groups in the order $C_2H_5 < CH_3 < OH$. The effect of a second group of the same or of a different kind is to decrease the effect of the first, and the simpler the group the more effective it is. Esters occupy an unexpected position. The aliphatic esters are much worse lubricants than their related acids or alcohols. Hydroxy-acids have a remarkably good lubricating power in the aliphatic series, but this is entirely lost in cyclic compounds. Generally, it is noted that no cyclic compound is a good lubricant. It is also shown that the better a lubricant is, the more strongly is it adsorbed by a metal surface. J. F. S.

Adsorption by Charcoal. I. Relation of Service Time to Adsorption and Absorption. H. H. Lowry and G. A. Hulett (*J. Amer. Chem. Soc.*, 1920, **42**, 1393—1408).—The adsorption of nitrogen, carbon dioxide, and water by a large number of different varieties of charcoal has been studied. It is shown that no relationship exists between the length of time the charcoal has been in use and the adsorption for gases, such as nitrogen and carbon dioxide. Differences in the method of preparation of the charcoal change the adsorptive capacity by as much as 100%. Nitrogen and carbon dioxide adsorbed by charcoal may be regarded as a condensed layer one molecule thick. Measurements of the isothermal adsorption of water at 25° show that there is no adsorption in the strict sense of the term, but that the water is held in the capillary tubes, that is, it is absorbed. Using Anderson's formula (A., 1914, ii, 632) connecting the radius of a capillary with vapour pressure, the mean diameters of the capillaries of four specimens of charcoal have been calculated, and are found to vary from $2 \cdot 8 \times 10^{-7}$ cm. to $9 \cdot 2 \times 10^{-7}$ cm. The maximum diameter of any of the charcoal examined was $1 \cdot 3 \times 10^{-6}$ cm. By means of the same formula and the absorption isothermals of

water, the surface of the charcoal is found to vary from 160 sq. metres to 436 sq. metres per gram. The variation of surface is not always accompanied by a corresponding variation in adsorptive capacity. This makes the conception of elementary spaces, as postulated by Langmuir, a necessity. There is no relationship between the volume of the capillaries and the time of use of the charcoal. The same is also true for the saturation point and the retentivity of the charcoal. J. F. S.

Adsorption by Charcoal. II. Relation of Oxygen to Charcoal. H. H. LOWRY and G. A. HULETT (*J. Amer. Chem. Soc.*, 1920, **42**, 1408—1419. Compare preceding abstract).—The adsorption of oxygen by charcoal has been examined with several varieties of charcoal. In the case of this gas, the behaviour is shown to be anomalous, due to the coupling of two phenomena, adsorption and surface combination. Charcoal has been heated in a furnace up to 1200° out of contact with oxygen-containing materials, and the evolved gases collected and analysed. The results point to the formation on the charcoal surface of a carbon–oxygen complex, which is essentially a stable solid oxide of carbon, at ordinary temperatures. This complex decomposes on heating into carbon monoxide and carbon dioxide, and can thus be considered to be an intermediate compound in the combustion of charcoal. This is supported by the views of Armstrong (A., 1904, ii, 948) and by the experimental work of Rhead and Wheeler (T., 1912, **101**, 831; **103**, 461), and by Langmuir (A., 1915, ii, 467). The amount of oxygen thus found to be combined in charcoal has been found to vary in two samples from 1·71% and 3·75% of the initial weight of the charcoal. J. F. S.

Solubility. II. Solubility Ratios of Salts in Strong Homoionic Solvents. J. N. BRÖNSTED (*J. Amer. Chem. Soc.*, 1920, **42**, 1448—1454. Compare this vol., ii, 294).—The solubility of potassium chloride, bromide, iodide, nitrate, chlorate, and iodate has been determined at 20° in solutions of potassium hydroxide of concentrations varying between 4·71*N* and 15·02*N*. The solubility of the haloids and the chlorate steadily decreases with increasing concentration of the hydroxide, that of the nitrate remains constant at the higher concentrations of hydroxide after decreasing with increasing hydroxide concentration, whilst the iodate decreases to an hydroxide concentration 11·10*N*, and then increases to 14·85*N*. The results are considered in the light of the views put forward in an earlier paper (*loc. cit.*). It is found that, taking the salts in pairs, the ratio of the solubility products is constant over a considerable range of hydroxide concentration, except in the case of the nitrate–chlorate ratio. The results indicate that the nitrate, chlorate, and iodate ions are equally hydrated. The salts investigated fall into groups: (1) the haloids and (2) the oxygen salts. The salts in either group exhibit similar behaviour as solutes, and are similarly hydrated and equally acted

on by electric forces in the solvent over a wide range of concentrations. J. F. S.

Hypophosphorous Acid. I. Its Ionisation Equilibria. Alec Duncan Mitchell (T., 1920, **117**, 957—963).

Polarity and Ionisation from the Point of View of the Lewis Theory of Valency. Wendell M. Latimer and Worth H. Rodebush (*J. Amer. Chem. Soc.*, 1920, **42**, 1419—1433).—A theoretical paper in which the conceptions of polarity and the ionisation of polar and non-polar compounds are considered on the basis of Lewis's valency hypothesis (A., 1916, ii, 310). Salts of elements which are not polar are ionised in solution by reacting with the solvent molecules or other molecules. The properties of an ionising solvent depend on the existence of moderately strong intermolecular fields. The dielectric constant is a measure of this type of polarity, but it has no significance with regard to highly polar compounds. J. F. S.

The Crystal Lattice. A. Reis (*Zeitsch. Physik.*, 1920, **1**, 204—220).—A method based on a pure geometrical conception of the space lattice is put forward to answer the questions of the nature of the existence of molecules and radicles in the crystal lattice. Application of this method to chemical compounds shows that a fundamental difference exists between the space lattice of salts and compounds not exhibiting a salt-like character. For chemical and crystallographic problems the method has many applications. It is shown that the distances between atoms in molecules and radicle ions are appreciably smaller than those between molecules. Classification of the kinds of lattices has been found to produce a homogeneous picture of the relation which exists between chemical constitution and cohesion forces, whilst the differences between these classes are readily shown by a consideration of the compressibility, hardness, and thermal expansion. The cohesion forces in all states of aggregation, as well as the association forces in liquids, are essentially the same, and result from pure electrostatic influences of the molecule. Those optical properties of salts which correspond with the mutual linking of ions are associated with the state of aggregation, whilst all other optical properties are independent of it. Both the heat of transition of polymorphous modifications and the heat of sublimation are distinctly less for molecular lattices than for ion lattices. In ion lattices, and only in these, the molecular union is raised and displaced by the lattice union. Chemical Abstracts.

Arrangement of Atoms in Crystals. W. Lawrence Bragg (*Phil. Mag.*, 1920, [vi], **40**, 169—189).—An examination of the distances between neighbouring atoms in a crystal leads to an empirical relation determining these distances. The distance between the centres of two atoms may be expressed as the sum

of two constants characteristic of the atoms. The arrangement of the atoms in a crystalline structure may therefore be pictured as that of an assemblage of spheres of appropriate diameters, each sphere being held in place by contact with its neighbours. This empirical law is summarised in a curve, in which the constants for a number of elements are plotted against the atomic numbers. The curve is periodic, and resembles Lothar Meyer's curve of atomic volumes. Each atom occupies a constant space in any crystalline structure of which it forms part. The space occupied by the alkali metals and the metals of the alkaline earths is greatest, that occupied by the halogens and electronegative elements least. The accuracy of the relationship is discussed. Variations of the order of 10% between the calculated and observed distances occur, so that the law is only approximately true. Nevertheless, it is of considerable assistance in the analysis of the more complex crystal structures, since the conception of the atoms as an assemblage of spheres of known diameters packed tightly together limits the number of possible arrangements which have to be tried in interpreting the diffraction of X-rays by the crystal. The physical significance of the relation is examined with reference to Langmuir's theory of atomic structure. From this point of view, it follows that two electronegative atoms are situated close together in a crystalline structure because they share electrons, and the spheres representing them are therefore assigned small diameters. On the other hand, an electropositive element does not share the electrons in its outer shell with neighbouring atoms, and is therefore situated at a distance from other atoms, so that it appears to occupy a greater space in the structure. It is shown that the relationship is less accurate when applied to the crystals of metals, which, on Langmuir's theory, consist of an assemblage of positive ions held together by electrons which have no fixed positions in the structure. From the distance between electronegative atoms holding electrons in common, an estimate is made of the diameter of the outer electron shell of the inert gases. The following values are given: neon 1·30 Å., argon 2·05 Å., krypton 2·35 Å., and xenon 2·70 Å. The atomic diameter of some thirty-eight elements is given, and the distance between the atoms in a large number of crystals. J. F. S.

Rate of Change of Distribution of Particles in a Colloidal System. A. Westgren (*Arkiv. Mat. Astron. Fysik*, 1918, **13**, No. 14, 18 pp.).—An experimental verification of Smoluchowski's formula for the rate of change of concentration of particles in a colloidal system, $\Delta^{-2}=2vP$, in which $P=(4/\alpha\pi)$

$$\int_{\sqrt{\alpha}}^{\infty}dR\int_{0}^{\sqrt{\alpha}}dr\int_{-1}^{+1}(e^{-R^2-r^2+2Rr\xi}/\sqrt{1-\xi^2})Rrd\xi,$$

$\alpha=a^2/4Dt$, and, according to Einstein, $D=(RT/N)(1/6\pi\eta r)$. This formula permits a determination of Avogadro's constant which leads to $N=60{\cdot}9\times10^{22}$, with a probable error of 5%.

Chemical Abstracts.

Distribution of Acetic Acid between Water and Charcoal. Alwyn Pickles (*Chem. News*, 1920, **121**, 49).—When acetic acid solutions are treated with charcoal, a large proportion of the acid is rapidly removed, but several hours are required for complete equilibrium to be attained. Relatively more acid is removed from dilute solutions, and the concentration of the acid in mols. per c.c. of charcoal varies with the kind of charcoal and its state of division. An increase of temperature over a long period, so that the surface and interior effects are complete, reduces the acid concentration of the charcoal, but over a short period increases it, owing to the acceleration of the still incomplete interior effect. Animal charcoal is an exception, since it removes the acid almost entirely by adsorption. In applying the distribution equation, $\frac{Cn \text{ Charcoal}}{C \text{ Water}} = K$, the values of n giving the most consistent values for K ranged from 1·76 to 2·6. The value for n (2·35) in Thorpe's "Dictionary of Applied Chemistry," vol. ii. (colloids), thus appears to be an average value. C. A. M.

Equilibrium between Chlorine, Plumbous Chloride, and Plumbic Chloride in Aqueous Solution. Ernest W. Wescott (*J. Amer. Chem. Soc.*, 1920, **42**, 1335—1349).—The equilibrium between solid plumbous chloride and chlorine in hydrochloric acid has been investigated with acid of concentrations down to the point where lead dioxide separates as a solid phase. The results show that the complex chloroplumbic acid has the composition $HPbCl_5$, for with a given chlorine pressure the quantity of this complex acid present in equilibrium with solid plumbous chloride was found to be proportional to the first power of the chloride-ion concentration. The hydrogen-ion concentration, which would not be involved in the equilibrium if the ionisation of the substances was complete, was found to have a small secondary effect, probably owing to an influence on the ionisation of the chloroplumbic acid. The equilibrium constant corresponding with the expression $(PbCl_5')/(Cl') . p_{Cl}$ is given by the expression $K' = 0{\cdot}055 + 0{\cdot}07c_H$, the concentrations being expressed in mols. per 1000 grams of water, the partial pressure of chlorine being given in atmospheres and the ionisations of hydrochloric acid and chloroplumbic acid being assumed equal. The equilibrium constant of the reaction $PbCl_2(s) + Cl_2(g) + 2H_2O = PbO_2(s) + 4H^{\cdot} + 4Cl'$, as given by the expression $K = (H^{\cdot})^4 . (Cl')^4 / p_{Cl_2}$ was found to be $2{\cdot}4 \times 10^{-5}$, under the assumption that the ionisation of the hydrochloric acid and the chloroplumbic acid is complete. From these equilibrium constants and from other data found in the literature, the values of the decrease of free energy at 25° were calculated for the case that the concentrations of all dissolved substances are molecular, except that of chlorine, the partial pressure of which is one atmosphere, and were found to be those expressed by the following free energy equations: $PbCl_2(s) + Cl_2(g) + Cl' = PbCl_5' - 6590$ joules, $PbCl_2(s) + 2H_2O + Cl_2(g) = PbO_2(s) + 4H^{\cdot} + 4Cl' - 43{\cdot}500$ joules, and $Pb(s) + O_2(g) = PbO_2(s) + 219{,}000$ joules. J. F. S.

The Kinetic Theory of Gases in the Light of the Theory of Relativity. RUDOLF MEWES (*Zeitsch. Sauerstoff. Stickstoff. Ind.*, 1920, **12**, 33—34; from *Chem. Zentr.*, 1920, iii, 70—71).—A connexion has not yet been established between the kinetic theory of gases or its laws and the theory of relativity developed by Lorentz, Gerber, Einstein, and Minkowski. The author's previous experiments and new calculations open the possibility of developing a dynamic theory of gases and vapours on the basis of the general law of action of mass. H. W.

Magnitude of the Atom. A. LANDÉ (*Zeitsch. Physik.*, 1920, **1**, 191—197).—A theoretical paper on the sphere of influence of the electrons. It is stated that the radius of the second electron ring of atoms having an atomic number in the neighbourhood of 10 is approximately $0·35 \times 10^{-8}$ cm. Values are given for the lattice constant, $\delta = 2r_+ + 2r_-$, for a number of alkali haloids. Here r_+ and r are the radii of the positive alkali- and the negative halogen-ions (or better of their spheres of influence). The following first approximations have been deduced for the diameters of the spheres of influence of a number of ions:

	Na_+.	K_+.	Rb_+.	Cs_+.	F_-.	Cl_-.	Br_-.	I_-.
$2r \times 10^8 =$	2·2	2·9	3·3	3·2	2·4	3·3	3·6	4·1

It is shown that $r_+/r_- = 0·68$ for eight electrons and $= 0·51$ for four electrons. That the value for the ratio for eight electrons is smaller than that calculated from the series of numbers given above, is explained on the ground that in the lattice the large halogen-ion spheres are more compressed than in the smaller alkali-ion spheres. CHEMICAL ABSTRACTS.

New Periodic Relationship between the Atomic Weights of the Chemical Elements. II. Law of Mirror Image Remainders. KARL FEHRLE (*Physikal. Zeitsch.*, 1920, **21**, 382—385. Compare this vol., ii, 303).—In a previous communication (*loc. cit.*) the author determined the difference between the ideal atomic weight and the actual atomic weight for the elements with atomic numbers 1—37. In the present paper the elements with atomic numbers 38—74 have been treated in the same way. The author now plots the differences as ordinates against the atomic numbers as abscissæ, and obtains an irregular curve which can be divided by a line at atomic number 37 into two halves which are exact mirror images of one another, that is, where a maximum is found in the first half of the curve, a minimum occurs in the same relative position in the second half of the curve and vice versa. It is shown that by means of this relationship doubtful atomic weight values may be checked and corrected. J. F. S.

General Isotopy. A. VAN DEN BROEK (*Physikal. Zeitsch.*, 1920, **21**, 337—340).—A theoretical paper, in which the general relationships of isotopes are discussed. It is shown that if the periodic

system were a system of only two series, for example, $3+4n$ and $4n$, without nucleus electrons, then atomic weight $=2Z$ and $2Z+1$ respectively, and all atomic weights would be whole numbers (Z is the atomic number). That this is not so is conditioned in the first place by the existence of at least two other series, $1+4n$ and $2+4n$, the atoms of which are less common. A table is drawn up of the whole of the elements on the basis of the above-named four series, and a system of isotopes on the $4\alpha/2\beta$ hypothesis is given for the elements with atomic numbers 29 to 35. J. F. S.

Nuclear Constitution of Atoms. Sir E. RUTHERFORD (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 374—400).—Bakerian lecture. A general discussion of previously published work on the constitution of the lighter atoms. Structures are put forward for carbon, nitrogen, and oxygen atoms. J. F. S.

A Force, apparently due to Mass, Acting on an Electron, and the Non-identity of Isotopes in Spectra and other Properties. WILLIAM D. HARKINS and LESTER ARONBERG (*J. Amer. Chem. Soc.*, 1920, **42**, 1328—1335).—A theoretical paper, in which the nature of isotopes is discussed. It is shown that isotopes may be distinguished by their spectra, and that there must be some difference, although small, between the other properties of isotopes.
J. F. S.

Glass to Metal Joints. E. C. MCKELVY and C. S. TAYLOR (*J. Amer. Chem. Soc.*, 1920, **42**, 1364—1377).—A résumé of the various metal glass joints described in the literature is given, and this is followed by a description of the method of making trustworthy joints between metal and glass. Two types of joint are described: (*a*) soldered joints, (*b*) fused joints. The first type of joint has only been used for joining tubes. A length of glass tube chosen so that it will fit easily inside the metal tube, is roughened for a length of 15—20 mm. and then coated with platinum by covering it with a suspension of platinum chloride in oil of lavender, and then burning off carefully in a bunsen flame. The metal tube is carefully coated with tin, solder, or lead. Using a slightly acid solution of zinc chloride as soldering flux, the metal tube is heated so that the tin is molten and the hot glass tube inserted and the whole allowed to cool slowly. Fused joints are made between metal and glass by means of the Kraus flux (equal weights of zinc oxide, borax, and powdered soda glass fused together). The metal tube is covered on its interior with a thin layer of the flux, the glass tube is flared out to a flat ring of a width equal to three times the thickness of the glass wall, and while hot pressed into the flux-lined metal tube. Fusion is completed by heating the outside of the metal tube in such a way that the glass is kept cool enough to prevent deformation. An account is given of the various types of apparatus for which these joints are applicable. J. F. S.

Equipment for Drying Ovens. C. W. FOULK (*J. Amer. Chem. Soc.*, 1920, **42**, 1454—1455).—The drying space in ovens is considerably augmented by removing the door and placing a number (three or four) drawers on each shelf, so that the whole oven space is filled with these easily removed drawers. The bottoms of the drawers are made of metal gauze, and the ease of use makes the back of the oven as convenient of access as the front. J. F. S.

Washing Bottles in Gas Works Laboratory Practice. H. J. HAILSTONE (*Gas World*, 1920, **72**, 376).—The inlet tube reaches to the bottom of the bottle and terminates in an upturned jet. Around it is a spiral tube, its lower end fitting over and being supported by the jet. An aperture should be left between the lower end of the spiral tube and the point of the jet, and for this purpose the lower end of the spiral tube is flattened, thus preventing the jet from completely closing the tube. In operation, the bottle is filled level with the top of the spiral with the solution, and the gas passed through it. The bubbles issue from the jet and ascend through the spiral carrying "plugs" of the solution with them, thus keeping the gas in contact with the liquid for a longer time. At the top of the spiral the gas passes out and the "plugs" of liquid fall back. Circulation of the liquid is thus made practically constant and the washing efficient. CHEMICAL ABSTRACTS.

Apparatus for Ultrafiltration. RICHARD GANS (*Ann. Physik*, 1920, [iv], **62**, 327—330).—An apparatus for rapid ultra-filtration is described. The principle of the present apparatus is the same as that of Bechhold (A., 1908, ii, 24, 823), but the construction is much simpler. Collodion filters are conveniently prepared by treating 12·5 grams of guncotton with sufficient absolute alcohol to moisten it, and then making the volume up to 500 c.c. with ether. A little of the solution is poured evenly on a glass plate, and when the ether has evaporated it is plunged into water to remove the filter from the glass. The filter is then washed in running water, and may be preserved in water containing a little chloroform or formalin. A more rapid filter is obtained when equal volumes of alcohol and ether are used in the preparation. The permeability of a filter can be varied by the addition of glacial acetic acid, but the permeability does not depend entirely on the quantity of acetic acid used, but also on the time which has elapsed between its formation and its use. J. F. S.

Inorganic Chemistry.

Solubility of Iodine in Hydriodic, Hydrobromic, and Hydrochloric Acids, and Formation of the Corresponding Polyhalogenated Acids. I. E. OLIVERI-MANDALÀ and A. ANGENICA (*Gazzetta*, 1920, **50**, i, 273—281).—The saturated

aqueous solution of iodine at 25° contains 0·0334% of iodine, or 0·00131 mol. per litre. The solubilities of iodine in solutions of various concentrations of hydriodic, hydrobromic, and hydrochloric acids have also been determined. It is found that the solubility of iodine in the halogen hydracid is equal to that in the solution of the corresponding potassium salt at the same concentration; the solubility of the iodine is hence specific to the halogen ion, and is independent of the nature of the positive ion of the halogen compound. The freezing points of hydriodic and hydrobromic acid solutions are unaltered by dissolution of iodine in these solutions. Further, if the existence of trihalogenated acids in dilute solution be assumed, it is found that the degree of dissociation of hydriodic acid in solutions of 0·1—0·3*N*-concentration is equal to that of the acid, HI_3; the same holds for HBr and HBr_3. T. H. P.

Distribution of Ozone in the Direct Current Corona. Eric K. Rideal and Jakob Kunz (*J. Physical Chem.*, 1920, **24**, 379—392).—The formation of ozone by various methods is considered theoretically in the light of the various radiation hypotheses, and the conclusion is drawn that molecular species of a given type may be activated to varying degrees by a given radiation. The distribution of ozone in a direct-current corona is experimentally examined. The corona was produced in a brass tube with quartz ends, a platinum wire being suspended centrally down the tube and connected to the positive pole of a current of 16,500 volts, whilst the brass tube is earthed. Oxygen was slowly passed through the corona, and samples were withdrawn at various points and analysed. To control the analyses, an optical analysis was also carried out by means of a beam of ultraviolet light and a photoelectric cell. It is shown that the distribution of ozone in the corona varies very notably with the sign of the discharge, the negative corona producing higher concentrations than the positive corona. The average yield of ozone obtained was 0·045 gram/coulomb at the negative corona and 0·024 gram/coulomb at the positive corona. The distribution of ozone in a direct-current positive corona differs in a marked manner from that in a negative corona. The ultraviolet light emission from the corona exceeds that of the visible light, and in the corona itself the ratio of ultraviolet light to visible light is exceedingly high. J. F. S.

Sulphur Dioxide as a Source of Volcanic Sulphur. Jacob Papish (*Proc. Indiana Acad. Sci.*, 1918, 170—171).—Sulphur dioxide is reduced to sulphur by methane at elevated temperature. The author suggests that sulphur occurring in volcanic regions may, in part, be formed by reduction of sulphur dioxide by methane, carbon monoxide, or hydrogen, all of which occur in volcanic exhalations. Chemical Abstracts.

Freezing-point Solubility Curve for Sulphur and Dichlorodiethyl Sulphide. J. A. Wilkinson, Christ Neilson, and H. M. Wylde (*J. Amer. Chem. Soc.*, 1920, **42**, 1377—1382). —The solubility of rhombic sulphur, monoclinic sulphur, and

amorphous sulphur has been determined in $\beta\beta'$-dichlorodiethyl sulphide over the temperature range 13·82—128°, and the solubility-freezing-point curves constructed. The solubility of rhombic and monoclinic sulphur is the same at all temperatures. Below 78°, the solid phase which crystallises is rhombic sulphur, whilst above that temperature monoclinic sulphur separates. The solubility of amorphous sulphur is less than 0·14% at temperatures below 120°. Saturated solutions of sulphur in dichlorodiethyl sulphide contain 7·6% of sulphur at 80°, 11·3% at 90°, 17·5% at 100°, and 21·0% at 104°. J. F. S.

The System Ammonia–Water. S. Postma (*Rec. trav. chim.*, 1920, **39**, 515—536).—The melting-point curve of the system ammonia–water shows the existence of two hydrates, NH_3,H_2O and $2NH_3,H_2O$, having m. p.'s $-79·0°$ and $-78·8°$ respectively. The boiling-point curves do not give any indication of the existence of these compounds.

The vapour-pressure curve of ammonia was determined, and is represented by the formula $\log p = 7·2379 - 1282·86/T$, from which the heat of vaporisation is calculated as 5864 cal. The vapour-pressure curves of mixtures of ammonia and water were constructed, and also the curve of sublimation of solid ammonia. W. G.

Oxidation of Arsenious Anhydride in Alkaline Medium in the Presence of Ferrous Sulphate. G. Gire (*Compt. rend.*, 1920, **171**, 174—176).—The absorption of oxygen by a solution of arsenious oxide and ferrous sulphate in the presence of sodium hydroxide varies with the amount of alkali present. The volume of oxygen absorbed at first diminishes as the amount of alkali increases, reaching a minimum when the alkali is slightly in excess of that required to form the arsenite, $Na_2As_2O_4$. It then increases to a constant maximum, when the amount of alkali present is slightly in excess of that required to form the arsenite, $Na_4As_2O_5$. If the amount of alkali present is kept constant, the oxygen absorbed is proportional to the amount of iron present, but is always in excess of that required to oxidise the ferrous salt to the ferric state. W. G.

Charcoal before the War. III. Wilder D. Bancroft (*J. Physical Chem.*, 1920, **24**, 342—366. Compare this vol., ii, 429). —A further discussion of the properties of charcoal. In the present paper, the oxidation of charcoal from various sources by various reagents is considered. J. F. S.

The Action of Extremely Finely Divided Gases. C Zenghelis (*Compt. rend.*, 1920, **171**, 167—170. Compare this vol., ii, 363).—A more detailed study of the reduction of carbon dioxide in the presence of water by hydrogen in a very finely divided state shows that the action steadily diminishes in velocity with the time. Although it takes place to some extent in the dark, it is markedly accelerated by sunlight, and still more so by

ultraviolet rays. In all cases, the formaldehyde first produced rapidly undergoes polymerisation. The reduction of carbon dioxide by hydrogen takes place slowly with both gases in solution in water without any passage of the hydrogen through a porous vessel.

W. G.

Some Sources of Helium in the British Empire. J. C. McLennan (*Bull.* No. 31, Dept. of Mines, Canada).—An account of the natural gases of Canada, British Columbia, New Zealand, New Brunswick, and England, which contain helium. The radioactivity and helium content are tabulated, and methods of estimation are described. [Compare T., 1920, **117**, 923; this vol., ii, 488, 508.]

J. F. S.

Application of the Laue Diagram to the Determination of the Structure of Calc Spar. Ernst Schiebold (*Leipziger Abh.*, 1919, **36**, 65—213; from *Chem. Zentr.*, 1920, iii, 123).—The investigation was undertaken with the object of elucidating suitable methods of determining indices and of applying the Laue diagram to a useful means of determining structure. The systematic procedure recommended gives results confirmatory of Bragg's structure model when applied to sodium chloride. The structure deduced for calc spar permits a satisfactory explanation of the cleavage relationships from Bragg's model.

H. W.

The Constituents Formed by Reciprocal Penetration of Zinc and Copper at a Temperature at which these Two Metals and all their Alloys are in the Solid State. H. Weiss (*Compt. rend.*, 1920, **171**, 108—111).—When zinc and copper were heated in close contact at 400° for two days, the following constituents were found in the contact layer: pure zinc or its solid solution, η; the constituent ϵ to a thickness of about 0·2 mm.; the constituent γ, thickness about 1 mm.; a very thin zone of the constituent β; and copper or its solid solution, α. If the duration of heating was increased to ten days, the thickness of the zones ϵ and γ increased without appreciable alteration of the zone β.

W. G.

System Zinc Oxide, Phosphoric Oxide, and Water at 25° and 37°. N. E. Eberly, C. V. Gross, and W. S. Crowell (*J. Amer. Chem. Soc.*, 1920, **42**, 1433—1439).—The equilibrium between zinc oxide, phosphoric oxide, and water has been determined at 25° and 37° over a long range of concentrations, and the equilibrium curves have been constructed. At 25° the solid phases, $Zn_3(PO_4)_2,4H_2O$, $ZnHPO_4,3H_2O$, and $Zn(H_2PO_4)_2,2H_2O$, separate, whilst at 37° an additional solid phase, $ZnHPO_4,H_2O$, is obtained. The tetrahydrate of normal zinc orthophosphate may be prepared by saturating a 50% solution of phosphoric oxide in water with zinc oxide at the boiling point. The water lost by evaporation is replaced and the mixture cooled in ice. About 10 volumes

of ice-cold water are added, and the solution vigorously stirred and poured through a filter into a large porcelain dish. The dish and its contents are heated on a water-bath with stirring, when a large quantity of shining plates of the tetrahydrate separate. $Zn_3(PO_4)_2,4H_2O$ crystallises in shining, orthorhombic plates; $ZnHPO_4,3H_2O$ forms sticky, thread-like crystals which agglomerate into cotton-wool-like masses; $ZnHPO_4,H_2O$ forms small, hard, transparent needles, which, since the extinction is oblique to the ong axis, are probably triclinic; $Zn(H_2PO_4)_2,2H_2O$ forms large, ransparent, triclinic rhombohedra. J. F. S.

New Method of Preparing Tripotassium Lead Hydrogen Octafluoride. Frank C. Mathers (*J. Amer. Chem. Soc.*, 1920, **42**, 1309—1311. Compare Clark, A., 1919, ii, 513).—Lead peroxide s readily attacked by 96% hydrofluoric acid, and a yield of 62% of lead tetrafluoride obtained. On dilution of the solution, the tetrafluoride is speedily hydrolysed, but this may be largely prevented by the addition of a little potassium or ammonium fluoride before dilution. Tripotassium lead hydrogen octafluoride, $3KF,HF,PbF_4$, is best prepared by fusing a mixture of equal weights of potassium hydrogen fluoride and lead peroxide in a platinum dish at 200°. The fluoride is melted and the dioxide slowly added, and the heating continued until the mass becomes pasty. After cooling, the mass is moistened with concentrated hydrofluoric acid, stirred with a carbon rod, and heated at 225° for several hours; after repeating the heating several times, the mass becomes practically white and contains 80—86% of the octafluoride. Pure crystals were obtained by digesting the crude residue with concentrated hydrofluoric acid, filtering, and crystallising. The pure salt is very easily hydrolysed, but the presence of a small excess of potassium fluoride retards the hydrolysis to a marked degree. The action of heat on the octafluoride does not give enough fluorine for the odour to be recognised, although the platinum dish was etched. J. F. S.

Crystal Structure of Ferromagnetic Metals. Albert W. Hull (*Physical Rev.*, 1919, **14**, 540—541).—Since the atoms of ferromagnetic materials are, in general, ferromagnetic only when in pure metallic condition and between definite limits of temperature, and the relative spacing of the atoms is apparently essential, it might have been anticipated that ferromagnetic metals would have the same crystal structure. That this is not the case is shown by the data on the type of lattice and the distance between atoms of chromium, iron, cobalt, and nickel (compare *ibid.*, 1917, **10**, 661). Nickel has the same crystal structure as copper, while cobalt appears in two forms, one like copper and one like magnesium. Neither is like iron. Chromium, which is not ferromagnetic, has a centred cubic arrangement, like iron. It is evident, therefore, that ferromagnetism does not depend on any particular arrangement of atoms. It is much more likely that it depends on

ie distance between the atoms, which would explain the fact that iis property is lost when the temperature is increased beyond a efinite value. CHEMICAL ABSTRACTS.

Catalytic Action of Copper Salts on the Oxidation of errous Compounds by Air. L. MAQUENNE and E. DEMOUSSY *'ompt. rend.*, 1920, **171**, 65—69).—Copper salts exert a marked atalytic effect on ferrous salts, favouring their oxidation in air. his effect is noticeable at extreme dilutions (1 in 100,000,000), id is sensitive to the least change in the reaction of the medium. is apparently independent of the degree of ionisation of the ixture of copper and ferrous salts, but is most marked with rrous salts of weak acids, being apparently related to their degree ' hydrolytic dissociation. W. G.

The Precipitation of Tin by Iron. N. BOUMAN (*Rec. trav. iim.*, 1920, **39**, 537—541).—By the addition of a solution of annous chloride, the potential of iron in a solution of ferrous iloride becomes less negative, so that it is then less electronegative ian tin; consequently it is no longer in the state to precipitate n from its solution. This result is discussed on the electronic ieory, and a satisfactory explanation given. At the same time, is shown that reduced iron will precipitate tin from its solution boiled with a slightly acid solution of stannous chloride.

W. G.

Zirconium. J. W. MARDEN and M. N. RICH (*J. Ind. Eng. Chem.*, 1920, **12**, 651—656).—Fairly pure (99·8%) zirconium oxide may be prepared from zircite by decomposing the mineral with sulphuric acid, precipitating the zirconium as basic sulphate, and igniting the precipitate. Good yields are also obtained by fusing zircite with sodium carbonate and hydroxide and precipitating zirconium oxide by means of sulphur dioxide, and by a method in which the zirconium is precipitated as phosphate. Potassium zirconium fluoride may be prepared in pure condition by dissolving zirconium dioxide in hydrofluoric acid, treating the solution with the calculated amount of potassium carbonate, and recrystallising the salt three times. Its solubility in water varies greatly with the temperature, 100 c.c. dissolving 25·0 grams at 100°, 15·0 grams at 18°, and 0·78 gram at 0°. The pure metal may be prepared from this salt or from the oxide. The coherent metal may be obtained by aluminothermic reduction, by heating the amorphous product, and (in admixture with carbide) by reducing zirconium oxide with carbon. The amorphous variety is obtained by reducing potassium zirconium fluoride by means of sodium or aluminium in an exhausted iron tube or a vacuum furnace. The coherent metal is much less chemically active than the amorphous variety, and, unlike the latter, is insoluble in all acids except aqua regia and hydrofluoric acid. A study of different analytical methods showed that zirconium is incompletely precipitated as fluoride, and that it is only quantitatively precipitated by peroxide when the concentra-

tion of the latter in the solution is high. The precipitation as phosphate is best effected in the presence of 10% of sulphuric acid, hydrogen peroxide being added to retain the titanium in solution. The quantity to be precipitated should not exceed 0·05—1 gram in 200 c.c., and the liquid should be heated to boiling point and allowed to remain after the addition of an excess of disodium hydrogen phosphate. In the case of solutions containing 10 to 20% of sulphuric acid, an excess of 50% of ammonium phosphate should be added. [See also *J. Soc. Chem. Ind.*, 1920, September.]

C. A. M.

Thorium and Uranium Content of Certain Minerals; the Gradual Transformation of Thorium-*B*–Thorium-*C*. STEFAN MEYER (*Sitzungsber. Akad. Wiss. Wien*, **128**, [2*a*], 897—908; from *Chem. Zentr.*, 1920, iii, 75).—The estimation of thorium or uranium in uranium ores containing very little thorium, or in thorium ores with a very small uranium content, cannot be effected by the usual methods; it is, however, relatively easy to estimate minimal amounts of uranium by the proportional radium content, and of thorium through its active precipitates. In a specimen of monazite sand, the ratio of thorium to uranium was 83:1, an extreme value, which is not commonly observed. A specimen of Joachimsthal pitchblende contained $6·64 \times 10^{-5}$ grams of thorium isotopes (thorium + ionium) for 1 gram of uranium, or $3·33 \times 10^{-7}$ grams of radium. The thorium content of a crystalline Morogoro uranium mineral, the uranium content of which was already known, was estimated in the following manner. The amount of thorium-*B* obtained under definite conditions from a known weight of the mineral was compared with the amount produced under identical conditions from a mineral of known thorium content. The Morogoro mineral was thus found to contain 0·53% of thorium and 74·5% of uranium. The amount of thorium is so great that the equivalent of the thorium–ionium from the mineral can scarcely be distinguished from that of thorium itself. In an appendix, the author gives tables showing the effect of differing exposure in thorium emanation on the activity of active thorium precipitates.

H. W.

Crystalline Structure of Antimony. R. W. JAMES and NORMAN TUNSTALL (*Phil. Mag.*, 1920, [vi], **40**, 233—239).—The crystal structure of antimony has been determined for antimony by means of an *X*-ray spectrometer, using a bulb with a palladium anti-cathode. The glancing angles for first-order spectra were as follows: (100), 5°27′; (110), 7°24′; (1$\bar{1}$0), 7°50′; (111), 4°26′; and (11$\bar{1}$), 19°14′. The intensities and the small glancing angle indicate that the underlying structure is a face-centred lattice, and that the unit rhomb contains eight atoms. The structure, as in the case of the diamond, consists of two interpenetrating face-centred lattices. The arrangement of the lattices can be seen, as follows. "Suppose for one of the lattices, diagonals are drawn parallel to the trigonal axis for each of the eight equal rhombo-

hedral cells into which the unit lattice may be divided. From considerations of symmetry, it is clear that the atoms of the second lattice must lie in these diagonals. If they lay at the unoccupied corners of the first lattice, the structure would become a simple rhombohedral one. This does not accord with the observed facts, but if the atoms of the second lattice are all displaced from these corners along the diagonals in the same direction by a distance equal to 0·074 of the length of the diagonal of one of the small cells, all the observed facts are explainable." J. F. S.

Revision of the Atomic Weight of Bismuth. Analysis of Bism th Chloride. O. HÖNIGSCHMID and L. BIRCKENBACH (*Sitzungsber. Akad. Wiss. München*, 1920, 83—86; from *Chem. Zentr.*, 1920, iii, 122).—With the object of discovering possible isotopes of bismuth, the authors have analysed and investigated bismuth chloride and bromide, using the methods of Richards and his co-workers. The ratio $BiCl_3:3AgCl$ was determined gravimetrically, and the ratio $BiCl_3:3Ag$ by gravimetric titration with the aid of the nephelometer. The first series gave the value Bi = 209·024, whilst the second set indicated Bi = 209·027; the mean, 209·026, is regarded as the present most probable value for the atomic weight of bismuth, and is a unit higher than that previously adopted. H. W.

[Salts with High Ammonia Content.] WALTER PETERS (*Ber.*, 1920, **53**, [*B*], 1143).—The formation of ammines containing more than six molecules of ammonia (Ephraim and Moser, this vol., ii, 378) has previously been observed by the author, who has obtained platinum double salts with 9, 12, 15, or 18 molecules (compare Peters, A., 1910, ii, 114). H. W.

Mineralogical Chemistry.

Pulverulent Mineral [Fluorite] from Dorgali, Sardinia. ENRICO CLERICI (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 309—312).—This mineral, which is shown by its physical and chemical properties to be fluorite, exhibits thermoluminescence, even under carbon tetrachloride or acetone, and emits radiations capable of influencing photographic plates and of penetrating glass, mica, or gelatin, but not aluminium or black paper. This phenomenon may be due to the presence of traces of rare earths. T. H. P.

Plumbiferous Barytes from Shibukuro, Japan. RYŌICHI ŌHASHI (*Min. Mag.*, 1920, **19**, 73—76).—The mineral is deposited

by a hot spring, the water of which has the following composition in parts per thousand: H 0·07500, K 0·02491, Na 0·04415, NH_4 0·00011, Ca 0·04870, Mg 0·01483, Fe 0·24846, Al 0·09622, Cl 2·69729, H_2SO_4 0·42034, SO_4 0·93776, HBO_2 0·04244, H_2SiO_3 0·37022; total, 5·02043; D^{19} 1·0030. In the rock fissures and at the orifice where the temperature is nearly 100°, the deposit consists of ordinary barytes, but in the stream of hot water, with a temperature of 40—50°, the crystalline deposit consists of plumbiferous barytes of the variety known as "hokutolite" (so named from the occurrence in the hot spring at Hokuto, in Formosa), together with sulphur, siliceous sinter, ferric oxide, realgar, and orpiment. It has the composition:

	BaO.	PbO.	SO_3.	Fe.	Ign.	Total.
I.	59·96	4·67	32·77	—	—	97·40
II.	48·95	17·78	32·24	trace	0·60	99·57

corresponding with A_1B_{14} and A_1B_3, whilst for the mineral from Hokuto the composition ranges from A_1B_3 to A_3B_5 (where A = anglesite, B = barytes). The optical characters are intermediate between those of anglesite and barytes, and this supports the suggestion that the mineral is an isomorphous mixture. The barytes, whether containing lead or not, is radioactive, ranging from 0·32 to $1·37 \times 10^{-10}$ curie units per gram of mineral. It also exhibits a self-luminescent effect, and when heated glows brilliantly (thermoluminescence). L. J. S.

Analyses of Dolomites. C. L. Harding, J. B. Shumaker, and
in thW. Rothrock (*Chem. News*, 1920, **121**, 50—52).—Twenty
under des are given of specimens (crystals and rocks) labelled as
compared'; some proved to be ordinary limestone or calcite, and in
from a mina sandstone (compare this vol., ii, 118). L. J. S.
was thus fou
The amount **nerals from the Wreck of a Fire-ship.** Arthur
thorium–ioniun. *Mag.*, 1920, **19**, 64—68).—Cavernous masses of
from that of thmixed with charcoal were taken up in 1846 from
tables showing thertly fused lead pump of a fire-ship which was
on the activity of uth Harbour in the year 1780. They show small
Crystalline Strunite ($PbCl_2$), anglesite ($PbSO_4$), leadhillite
Norman Tunstall (O), and galena (PbS). These were evidently
crystal structure of on of sea-water on the lead. L. J. S.
by means of an *X*-ray
anti-cathode. The g **Parco Chigi, Ariccia, Rome.** Francesco
follows: (100), 5°27 (*Riv. Min. Crist. Ital.*, 1917, **48**, 52—64).—
and (11$\bar{1}$), 19°14′. y suitable for analysis was supplied by clear,
indicate that the un from a volcanic bomb consisting mainly of
that the unit rhomactive indices, ω_{Na} = 1·5417, ϵ_{Na} = 1·5382, etc., are
the case of the dit for nephelite. D^{21} 2·65.
centred lattices. T₃.

	CaO.	MgO.	Na_2O.	K_2O.	Cl.	SO_3.	H_2O.	Total.
follows. "Supposes	2·15	0·06	14·48	5·73	trace	0·29	0·15	99·69

parallel to the trig

This gives the ratios $SiO_2:Al_2O_3:RO=2\cdot12:1:1\cdot01$. Deducting $K_2Al_2Si_2O_8$ and $(Ca,Mg)Al_2Si_2O_8$, and plotting the remaining SiO_2, Al_2O_3, and Na_2O on a triangular diagram, all recent analyses of nephelite fall on a line between the limits $Na_2Al_2Si_2O_8$ and $Na_2Al_2Si_3O_{10}$, the present analysis being nearest to the latter. The differences in composition of nephelite are explained by mixtures of these four molecules, but which of them exerts an influence on the variations in refractive indices could not be determined.

L. J. S.

So-called Hydrocastorite from Elba. PRODO CONVUCCI (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 264—267).—Doubts have been cast by Manasse (A., 1902, ii, 90) and D'Achiardi (A., 1906, ii, 555) on Grattarola's view that hydrocastorite represents a definite mineral species (A., 1878, 119). The author's analysis of Grattarola's mineral gives the percentage composition:

H_2O.	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	Na_2O+K_2O (by difference).
16·60	56·63	18·73	0·42	5·56	2·04

From these results and from the physical properties of the mineral the author draws the conclusion that it represents, not a definite mineral, but either a mixture of certain secondary minerals of uncertain and varying composition or, sometimes, simply somewhat impure stilbite T. H. P.

Olivine from Etna. FRANCESCO STELLA STARRABBA (*Mem. Classe Sci. R. Accad. Zelanti, Acircale*, 1917, [iii], **9**, 41—65).—Small crystals occurring in tuffs are separated according to colour and crystal-habit into: I, olivine of a clear green colour and fairly transparent, D 3·42, γ_{Na} 1·707; II, hyalosideritic olivine of a dark brownish-green colour and almost transparent, D 3·56, γ_{Na} 1·7303. Analysis I corresponds approximately with

$$4(Mg,Ca)_2SiO_4,(Fe,Mn)_2SiO_4,$$

and II with $7(Mg,Ca)_2SiO_4,3(Fe,Mn)_2SiO_4$. The frequent presence of ferric oxide in volcanic olivine is commented on.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	Cr_2O_3.	FeO.
I.	37·07	0·05	1·01	5·24	—	14·26
II.	37·43	0·57	0·71	5·82	trace	19·34

	(Co,Ni)O.	MnO.	CaO.	MgO.	H_2O ?	Total.
I.	—	0·32	0·54	40·71	0·34	100·44
II.	0·11	0·64	1·00	34·43	0·14	100·19

L. J. S.

"Titanolivine" from the Ala Valley, Piedmont. F ZAMBONINI (*Bull. Soc. franç. Min.*, 1919, **42**, 250—279).—"Titanolivine" is of frequent occurrence in the serpentine rocks of the Alps, and its presence accounts for the wide diffusion of titanium in these rocks. Dark reddish-brown crystals found at several places in the Ala valley agree in their crystallographic

constants ($a:b:c=1.0735:1:5.667$, $\beta=89°59\frac{1}{2}'$) and optical orientation with clinohumite, but they differ chemically from this in containing some titanium and also hydroxyl in place of fluorine. Analysis gave:

SiO_2.	TiO_2.	PbO.	Fe_2O_3.	Al_2O_3.	GlO.	FeO.	MnO.	NiO.	MgO.
36·83	1·92	0·14	0·42	0·07	1·30	4·90	0·28	0·07	51·53

CaO.	K_2O.	Na_2O.	H_2O (<110°).	H_2O (>110°).	F.	Total.
0·03	0·09	0·03	0·05	2·99	0·03	100·68

corresponding with the ratios $SiO_2+TiO_2:RO:H_2O(+F)=1:2.23:0.26$, and with the formula $4Mg_2SiO_4,Mg(OH)_2$. The mineral is decomposed by hydrochloric acid. Water is expelled only at a high temperature. Glucinum has been previously detected in a mineral of this group by Jannasch and Locke (A., 1894, ii, 459), but lead is unusual. The earlier analyses of "titanolivine" by A. Damour (1855 and 1879) and G. Anelli (A., 1905, ii, 176) agree with the clinohumite formula only when it is assumed that titanium replaces magnesium, and they are probably at fault. The name "titanolivine" being thus inadmissible for this mineral, *titanhydroclinohumite* is suggested as an alternative. L. J. S.

Analytical Chemistry.

Method of Stating Analytical Results. A. Thiel (*Chem. Zeit.*, 1920, **44**, 525—526. Compare this vol., ii, 187).—The author suggests a nomenclature for equivalent or molecular quantities, for example, "norm" (symbol gN) for gram-equivalent, "mol" (gM) for gram-molecule, etc. W. P. S.

The Significance of the "Specific Refraction" for Analytical Chemistry. N. Schoorl (*Rec. trav. chim.*, 1920, **39** 594—599).—The specific refraction, $(n-1)/d$, may serve as a confirmatory measurement for the identification of an unknown organic compound, but its application is somewhat limited. W. G.

Fluoremetry. Quantitative Analysis by Comparative Fluorescence. L. J. Desha (*J. Amer. Chem. Soc.*, 1920, **42** 1350—1363).—A new method of micro-analysis is described, of the same order of sensitiveness as colorimetry and nephelometry, which should prove generally applicable to the estimation of minute quantities of the considerable number of substances which are either fluorescent themselves or may be rendered so by the addition of a suitable reagent. Ultraviolet rays from a quartz mercury

lamp are filtered from most of the visible radiation and used to excite fluorescence in solutions of such substances contained in the comparison cylinders of the Kober nephelometer. The intensity of the fluorescent light thus produced, as observed in the eyepiece of the instrument, is equalised in the usual manner by altering the heights of the exposed columns. For sufficiently dilute solutions, the curves obtained by plotting the scale readings against concentrations are quite regular. These calibration curves are drawn for solutions containing 0·5—2 mg. per litre of quinine sulphate in *N*-sulphuric acid, and for solutions of 2—4 mg. per litre of aniline iodoeosin in *N*/10-alkali. Such a curve differs from that of inverse proportionality (the colorimetric curve) much more than from one drawn according to the nephelometric formula. Some peculiarities of the latter are indicated, and it is shown that when two constants are used (one for solutions stronger than the standard and the other for those more dilute), the values corresponding with the fluoremetric readings may be taken from the nephelometric curve with an average error of 1%. J. F. S.

A Gas Analysis Apparatus Accurate to 0·001% mainly designed for Respiratory Exchange Work. August Krogh (*Biochem. J.*, 1920, **14**, 267—281).—The apparatus contains two improvements on the usual arrangements. The more important of these is the use of three separate gas burettes, the first being used exclusively for moving the air to and from the absorption pipettes, the second being of a size suitable for measuring the air before and after the absorption of carbon dioxide, and the third is for measuring the air after the absorption of oxygen. The water vapour necessary for saturating the sample of air, after it comes from the absorption pipettes, is supplied by the first burette. The other two burettes contain just enough water to ensure that the samples remain saturated.

The second improvement is that the mercury is raised and lowered in the burettes, not by raising and lowering a mercury reservoir, but by means of air pressure. This obviates the use of rubber connexions between the burettes and the reservoirs, and also considerably facilitates the analytical manipulations.

The apparatus is fully sketched in the original, and detailed instructions are given for conducting an analysis. W. G.

Titration with the Hydrogen Electrode. W. D. Treadwell and L. Weiss (*Helv. Chim. Acta*, 1920, **3**, 433—446).—The authors describe a hydrogen electrode which, when in steady use, retains its activity for six weeks, and is then easily regenerated. The change in potential of the electrode during acidimetric titrations may be measured with sufficient accuracy by means of a millivoltmeter, and it may be used for the titration of both strong and weak acids. With the latter, the equilibrium constants may be calculated very simply from the fall in potential during the

titration. Strong acids in presence of weak acids may also be estimated. T. H. P.

Standardisation of Sodium Thiosulphate, Arsenious Acid, Potassium Bromate, Potassium Iodate, etc., Solutions by means of Standard Sulphuric Acid Solution. L. BERTIAUX (*Ann. Chim. anal.*, 1920, [ii], **2**, 207—208).—The equivalent quantity of iodine liberated from a mixture of potassium iodate and potassium iodide by a definite volume of standard sulphuric acid solution is used for the standardisation of thiosulphate and arsenious acid solutions. Variations of the reaction are employed for the standardisation of the other solutions mentioned. W. P. S.

Indicators used for Estimating Free Acid in Pickling Solutions. C. L. BOYLE (*J. Ind. Eng. Chem.*, 1920, **12**, 571—572). —Sodium or potassium thiocyanate solution is recommended as the indicator, since the end-point shown by ordinary indicators is obscured by the large amount of ferrous sulphate present in the pickling solution. W. P. S.

The Incineration of Organic Substances Prior to Analysis for the Mineral Elements which they Contain. Application to the Analysis of Blood. A. DESGREZ and J. MEUNIER (*Compt. rend.*, 1920, **171**, 179—182).—For the incineration of organic substances for subsequent ash analysis, the authors recommend that the material should first be thoroughly dried, and then ignited and allowed to burn at as low a temperature as possible. In this way, a carbonised material is obtained which, when further incinerated, readily becomes incandescent and leaves a white ash. If excess of alkali salts is present, these should be extracted with water before the final incineration. This method has been applied to the ash analysis of blood, and the presence of copper, manganese, and lithium detected. W. G.

Volumetric Estimation of Sulphuric Ions. JOSEPH ERLICH (*Ann. Chim. anal.*, 1920, [ii], **2**, 214—215).—The solution, containing about 0·01 gram of sulphuric acid as alkali salt, is neutralised, boiled with the addition of barium carbonate, set aside for twelve hours, filtered, the precipitate washed, and the alkalinity of the filtrate titrated with $N/10$-acid. The alkalinity is equivalent to the sulphuric ions present originally. W. P. S.

Estimation of Nitrate Nitrogen in Nitrates and Fertilisers. H. C. MOORE (*J. Ind. Eng. Chem.*, 1920, **12**, 669—673).—From 0·8 to 1·7 gram of the sample, according to the quantity of nitrate present, is mixed with 35 c.c. of sulphuric acid containing 1 gram of salicylic acid, the mixture is shaken for fifteen minutes, 5 grams of sodium thiosulphate are added, and the mixture heated until frothing ceases. Five grams of potassium sulphate and 0·5 gram

of mercury are then added, and the heating is continued for ninety minutes after a clear solution has been obtained. Sodium sulphide is added in the subsequent distillation of the ammonia.

W. P. S.

Preparation of Diphenylamine-sulphuric Acid. FR. HAHN (*Zeitsch. Nahr. Genussm.*, 1920, **39**, 355—356).—The sulphuric acid used in preparing diphenylamine reagent for the detection of nitrates should be free from nitric acid, as shown by the brucine test. Sometimes the reagent made with sulphuric acid free from nitric acid becomes blue in colour after a short time; this is due to the presence of ferric salts in the sulphuric acid. Such acid may still be used if it is heated previously to boiling and then cooled; the ferric salts are reduced permanently by this treatment, and the acid does not give a blue coloration when mixed with diphenylamine. The course of the reduction may be followed by adding a trace of permanganate before heating the acid. The permanganate is also reduced, and the presence of the manganese tends to increase the sensitiveness of the reagent. W. P. S.

Iodic Acid as a Characteristic Microchemical Reagent for Gaseous Ammonia. GEORGES DENIGÈS (*Compt. rend.*, 1920, **171**, 177—179).—When one drop of a 10% aqueous solution of iodic acid is exposed to an atmosphere containing ammonia, it immediately becomes covered with a crystalline film. These crystals may readily be identified under the microscope as flattened, quadratic crystals of the normal iodate, NH_4IO_3. None of the volatile amines examined gave this reaction under these conditions. For the detection of traces of ammonium salts in a solution, the latter is first concentrated by evaporation, and then the ammonia is liberated by the action of magnesium oxide and tested as above.

W. G.

The Technique of the Estimation of Phosphoric Acid as Barium Phosphomolybdate. S. POSTERNAK (*Bull. Soc. chim.*, 1920, [iv], **27**, 564—568).—Very full details are given for preparing the solutions for, and conducting an estimation by, the method already described (this vol., ii, 505). W. G.

Estimation of Solvent Carbon Dioxide in Water. H. NOLL (*Zeitsch. angew. Chem.*, 1920, **33**, i, 182—184).—It was shown by Tillmans and Heublein (A., 1913, ii, 51) that free carbon dioxide in soft water has a much greater solvent action on calcium carbonate than the same amount of carbon dioxide in hard water, since that portion required to keep calcium hydrogen carbonate, etc., in solution has no solvent action on calcium carbonate. Curves plotted by Tillmans and Heublein enable the amount of solvent carbon dioxide to be read directly when the amounts of free and combined carbon dioxide are known. In the case of waters containing iron hydrogen carbonate, the semi-combined and the combined

carbon dioxide in the iron compound are titrated simultaneously with the free carbon dioxide, and, as a correction, 1·1 mg. of carbon dioxide must be deducted for each mg. of ferric oxide present. For this reason, the filtrate from plants used for removing iron from water will often yield higher values for free carbon dioxide than the original water. The combined carbon dioxide in water may be estimated by titration with hydrochloric acid, with methyl-orange as indicator, and also by boiling the water with excess of acid and titrating the excess, with phenolphthalein as indicator. The carbon dioxide in combination with iron is estimated by the first method, but not by the second. The results for solvent carbon dioxide in waters free from iron are most trustworthy when, in addition to calcium hydrogen carbonate, the water also contains considerable quantities of the hydrogen carbonates of magnesium and sodium. The solvent action of free carbon dioxide is probably reduced to the greatest extent by iron hydrogen carbonate, and successively less by the hydrogen carbonates of calcium, magnesium, and sodium.

C. A. M.

Hæmato-respiratory Functions. II. The Henderson-Morriss Method for Determining the Carbon Dioxide in Plasma and in Whole Blood. HOWARD W. HAGGARD (*J. Biol. Chem.*, 1920, **42**, 237—244).—A careful study of the Henderson-Morriss method (A., 1917, ii, 506) of determining the carbon dioxide of plasma or whole blood, and a comparison with the method of Van Slyke and Cullen (A., 1917, i, 521), show that the various corrections almost exactly neutralise each other. At ordinary temperatures and barometric pressures, the reading on the gas burette for the carbon dioxide absorbed during the gas analysis (corrected only for the carbonate of the ammonia solution) may be taken as indicating directly, within the error of the method, the amount of carbon dioxide contained in the blood or plasma. With this method, the analysis of whole blood is as easy as that of plasma.

W. G.

Estimation of Potassium and its Separation from Sodium by means of Sodium Cobaltinitrite. P. WENGER and C. HÉMEN (*Ann. Chim. anal.*, 1920, [ii], **2**, 198—199).—The potassium sodium cobaltinitrite precipitate, obtained in the usual way, is dissolved in hydrochloric acid, and the cobalt then estimated electrolytically or gravimetrically. The precipitate has the composition

$$K_2NaCo(NO_2)_6,$$

and the potassium may be calculated from the weight of cobalt found.

W. P. S.

Titration of Ammonium Hydrogen Fluoride. WALLACE S. CHASE (*J. Ind. Eng. Chem.*, 1920, **12**, 567—568).—Methyl-orange, litmus, lacmoid, methyl-red, and cochineal are untrustworthy as indicators in the presence of free hydrofluoric acid, and ammonia interferes with the sensitiveness of phenolphthalein. If,

however, the ammonium hydrogen fluoride solution is treated with an excess of calcium chloride, the hydrochloric acid liberated may be titrated, using methyl-orange as indicator. There is no need to remove the precipitated calcium fluoride by filtration.

W. P. S.

Estimation of Calcium by Different Methods. GEORGE E. ÉWE (*Chem. News*, 1920, **121**, 53—56).—The following average results were obtained in the estimation of calcium in a sample of calcite by different methods: (1) precipitation as calcium oxalate and weighing as calcium carbonate, 99·57%; (2) precipitation as calcium carbonate and weighing as such, 100·07%; (3) liberation of carbon dioxide with hydrochloric acid and weighing the carbon dioxide in potassium hydroxide solution, 100·03%; (4) precipitation as calcium oxalate and weighing as calcium oxide, 99·86%; (5) precipitation as calcium sulphate and weighing as such, 99·68%; (6) precipitation as calcium oxalate and weighing as calcium sulphate, 100·39%; (7) precipitation as calcium oxalate and titration with potassium permanganate, 99·68%; (8) precipitation as oxalate from a slightly acid solution, 99·87%; (9) liberation of carbon dioxide and calculation of loss into $CaCO_3$, 99·80%; (10) residual titration method, 99·75%. The theoretical amount of calcium (as $CaCO_3$) in the material was 99·959%. C. A. M.

Acidity and Acidimetry of Soils. III. Comparison of Methods for Estimating Lime Requirements of Soils with Hydrogen Electrode. IV. Proposed Method for Estimation of Lime Requirements of Soils. HENRY G. KNIGHT (*J. Ind. Eng. Chem.*, 1920, **12**, 559—562).—The vacuum method (A., 1916, i, 459) appears to be the most trustworthy for estimating the lime requirement of soils, and the hydrogen electrode method (this vol., i, 587) yields results which agree with those given by the vacuum method, provided that the soil is shaken with lime for more than three hours before the hydrogen-ion concentration is determined. The Hopkins (A., 1916, i, 459) and hydrogen electrode methods are the best for measuring the reduction of acidity in limed soils. A method proposed for estimating the lime requirements of soils consists in boiling a mixture of 10 grams of the soil, 25 c.c. of normal potassium chloride or sodium chloride solution, and an excess of calcium carbonate for ten minutes, and measuring the volume of the carbon dioxide evolved. The results obtained agree with those found by the hydrogen electrode method. W. P. S.

Rapid Identification of the Two Ionic Elements of Barium Sulphate. G. DENIGÈS (*Bull. Soc. chim.*, 1920, [iv], **27**, 560—564).—A more detailed account of work already published compare this vol., ii, 398). W. G.

Estimation of Lead in Chemicals in Acid Solution. NORMAN EVERS (*Pharm. J.*, 1920, **105**, 85—86).—In the colorimetric (sulphide) estimation of lead in acid solution, the test

solution and the comparison solution should have the same hydrogen-ion concentration, otherwise the colorations obtained are not comparable. The author recommends that the acidity should be neutralised before the sulphide is added, and that bromo-phenol-blue (tetrabromophenolsulphonphthalein) should be used as the indicator; this indicator is colourless at the neutral point. Iron does not interfere under these conditions, and the effect of copper may be prevented by the addition of cyanide. If both iron and copper are present, the copper should be separated by adding alum solution and ammonia, collecting the aluminium hydroxide (this precipitate also contains the lead), dissolving it in acid, and treating this solution as described, but without the addition of cyanide.
W. P. S.

Estimation of Mercury in Organic Combination by means of Zinc Filings. MAURICE FRANÇOIS (*Bull. Soc. chim.*, 1920, [iv], **27**, 568).—A simplification of the method previously described (this vol., ii, 269), which avoids the necessity for heating. About half a gram of the dry, powdered organic matter is weighed into a tared, conical flask. To it is added 30 c.c. of ether, 10 c.c. of alcohol, 1 c.c. of concentrated hydrochloric acid, and immediately, 1 gram of zinc turnings. The mixture is shaken once and left for half an hour. Another gram of zinc is added, the mixture shaken, and again left for half an hour, when a third gram of zinc is added, and the mixture left twenty-four hours. By this time all the mercury is deposited on the zinc, and the estimation is continued as described (*loc. cit.*). W. G.

Modification of Caron and Raquet's Reaction for Manganese. G. DENIGÈS (*Ann. Chim. anal.*, 1920, [ii], **2**, 215—216).—This reaction (A., 1919, ii, 351, 438) may be simplified as follows: 5 c.c. of the manganese solution and a few drops of sodium hydroxide solution are shaken thoroughly in a test-tube until a brown coloration is obtained; saturated oxalic acid solution is then added drop by drop. The brown coloration disappears and the characteristic red coloration develops. W. P. S.

The Use of Phenolphthalein and Diphenylamine in the Method with Persulphate for the Estimation of Manganese D. H. WESTER (*Rec. trav. chim.*, 1920, **39**, 600—602. Compar this vol., ii, 451).—The author finds that the use of an alkalin solution of phenolphthalein as a comparison solution, and diphenylamine for deepening the colour, in the estimation manganese colorimetrically, as recommended by Tillmans ar Mildner (A., 1915, ii, 583), does not give exact results. W. G.

Estimation of Manganese in Biological Material togeth with Data on the Manganese Content of Human Blo and Tissues. CLARENCE K. REIMAN and ANNIE S. MINOT (*J. B Chem.*, 1920, **42**, 329—345).—For the preliminary preparation

he tissue or blood, by means of which any manganese present is onverted into the sulphate, the authors recommend either a modifiation of Bertrand's method (compare A., 1912, ii, 459, 662), the usion with potassium acid sulphate being carried out at 500—600° n quartz vessels, or the digestion with sulphuric, nitric, and hydrohloric acids in pyrex Kjeldahl flasks. It is noted that quartz essels are liable to contain manganese, and must be tested by a reliminary fusion. For the conversion of the manganese sulphate nto permanganate, the authors further slightly modify Bertrand's odification (*loc. cit.*) of Marshall's method (compare *Chem. News*, 901, **83**, 76) with potassium persulphate.

A series of results is given for the manganese content of human lood, the values obtained varying from 0·004 to 0·02 mg. per 00 grams, most of the cases coming between the limits 0·01 and ·02 mg. No abnormality in manganese content was shown by the ew pathological cases examined, except, perhaps, in the case of yphilis of long duration, where the manganese is low.

The results for the manganese contents of human organs from ourteen autopsies are given, manganese being invariably present. he liver has the highest manganese content, 0·17 mg. per 100 rams of wet tissue on the average. W. G.

Estimation of Small Quantities of Iron as Thiocyanate. ICHARD WILLSTÄTTER (*Ber.*, 1920, **53**, [*B*], 1152—1154).—Small amounts of iron, such as are found in peroxydase preparations, can be estimated rapidly and accurately in the following manner. The solution under investigation (0·5—1 c.c.) is treated with concentrated hydrochloric acid (0·5 c.c.) and made up to 50 c.c. with freshly prepared ammonium thiocyanate solution (40%, or, with larger quantities of iron, 10%). The coloration is matched by the use of standard solutions of iron, which are similarly treated. Difficulties are caused by the presence of iron in the purest commercial ammonium thiocyanate and by the instability of ferric thiocyanate in solution; the latter effect is due to the gradual reduction of the ferric salt by the thiocyanate, but the process does not appear to be catalysed by the ferrous salt formed. The difficulty first named is overcome by boiling the ammonium thiocyanate solution for a short time, after which it remains colourless when cooled. H. W.

Use of Potassium Xanthate for the Detection and Separation of Cobalt in the Presence of Nickel. LOUIS COMPIN (*Bull. Sci. Pharmacol.*, 1920; from *Ann. Chim. anal.*, 1920, [ii], **2**, 218—220).—When a solution containing nickel and cobalt is acidified with hydrochloric acid and treated with a slight excess of potassium xanthate, the two metals are precipitated as xanthates. On the addition of ammonia, the nickel compound dissolves to give a blue solution, whilst the cobalt compound remains insoluble. When this method is used for the estimation of cobalt in nickel,

the ammoniacal solution of the cobalt compound should be acidified with hydrochloric acid, and the precipitation repeated in order to recover a trace of cobalt which dissolves in the ammonia.

W. P. S.

Estimation of Zirconium and Titanium in Zirconium Ores. G. E. F. LUNDELL and H. B. KNOWLES (*J. Amer. Chem. Soc.*, 1920, **42**, 1439—1448).—A method of estimating zirconium, titanium, and the total rare earths in zirconium ores, is described. The method is found to be applicable in the presence of any or all of the elements which have ever been found in zirconium ores.

Four grams of borax are fused and allowed to solidify in a platinum crucible, 0·3 gram of finely powdered ore (100 mesh) added, and the mixture heated over a Meker burner and stirred with a platinum rod for thirty minutes. The cooled mass is placed in hydrochloric acid (1:5) in a beaker and warmed on a steam-bath. The solution is transferred to a platinum dish, treated with sulphuric acid (1:20), and evaporated until fumes of acid are evolved. The concentrated liquid is cooled, diluted to 100 c.c., and the impure silica filtered off and washed, and the washings added to the filtrate. The filtrate is warmed overnight to precipitate small amounts of phosphorus as zirconium phosphate. The precipitate is filtered and washed with 5% ammonium nitrate, and the washings added to the filtrate. Ammonium chloride (5 grams) is added to the filtrate, followed by an excess of ammonia, and the solution boiled for a few minutes, filtered, and the precipitate washed with 2% ammonium nitrate, and the filtrate discarded. The precipitate is dissolved in hot 5% sulphuric acid and the paper thoroughly washed (solution *A*). The filter paper, together with the filter papers containing the silica and the zirconium phosphate, is ignited in the original crucible, the ash moistened and treated with 1 c.c. of sulphuric acid and 5 c.c. of hydrofluoric acid, and ignited until all the sulphuric acid is expelled. The residue is ignited with a small amount of sodium carbonate. The fused mass is digested with water and filtered. The residue is well washed with hot water, ignited, and fused with sodium hydrogen sulphate; the cooled fusion is dissolved in 5% sulphuric acid, and the solution added to the solution *A*. The foregoing treatment removes phosphoric acid and recovers any zirconium which was present in the silica. The solution containing the whole of the metals is neutralised until it contains about 1% (by volume) of free sulphuric acid, treated with hydrogen sulphide, and filtered if necessary. The filtrate is made up to 200 c.c., treated with tartaric acid in amount equal to five times the weight of the bases in solution, made ammoniacal, and saturated with hydrogen sulphide, and any sulphide filtered off. The acidity of the solution is brought to 10% of sulphuric acid in a volume of 400 c.c., the solution boiled to expel hydrogen sulphide, and cooled to 4—15°. An excess of a cold 6% aqueous solution of cupferron is added. An excess is indicated by a fine, white precipitate, wh

redissolves, instead of a curdy one, which remains. After digesting for five minutes, the precipitate is filtered with gentle suction, washed with 10% (by volume) hydrochloric acid, and dried. The paper and precipitate are ignited in a weighed platinum crucible over a blowpipe flame, and weighed. The weight is that of the oxides of zirconium, titanium, and the rare earth metals. After weighing, the oxides are fused with potassium hydrogen sulphate, taken up with 10% (by volume) sulphuric acid, and diluted to exactly 100 c.c. This is divided into two 50 c.c. portions, and the titanium estimated in one and the rare earths in the second, and the zirconium obtained by difference. *Estimation of titanium.*—If the content of titanium is low, it is estimated by Weller's colorimetric method, whilst if it is high, it is reduced to the sesquioxide in a Jones' reductor containing ferric alum and phosphoric acid in the receiver, and then oxidised to the dioxide by titration with potassium permanganate. *Estimation of the rare earths.*—The hydroxides are precipitated with excess of potassium hydroxide, filtered, washed, and then washed into a platinum dish with 5% hydrofluoric acid. The solution is evaporated nearly to dryness and treated with 5 c.c. of 5% hydrofluoric acid. If no precipitate is present, the rare earths are absent; if present, it is filtered, washed with 5—10 c.c. of the same acid, transferred to a platinum dish, and ignited. Sulphuric acid is then added, and the whole evaporated to dryness, dissolved in dilute hydrochloric acid, and the rare earth hydroxides precipitated with ammonia, filtered, washed, redissolved in hydrochloric acid, and evaporated to dryness The residue is treated with 5 c.c. of boiling 5% oxalic acid solution, and, after digesting for fifteen minutes, filtered, washed with 20 c.c. of 5% oxalic acid, ignited, and weighed. The accuracy of the method is shown by a series of concordant analyses of diorite to which weighed amounts of zirconium, titanium, thorium, cerium, and phosphate had been added. J. F. S.

Estimation of Zirconium in Steel. G. E. F. Lundell and H. B. Knowles (*J. Ind. Eng. Chem.*, 1920, **12**, 562—567).—A critical review of methods published previously. The authors also give a method for the estimation of silicon, aluminium, titanium, and zirconium in steels which may contain other elements, such as tungsten, chromium, vanadium, phosphorus, molybdenum, copper, nickel, cobalt, uranium, and cerium. The steel is dissolved in hydrochloric acid with the addition of nitric acid, silica is separated, the greater part of the iron removed by extraction with ether, the hydrochloric acid solution then treated with excess of sodium hydroxide, and the precipitate collected. This precipitate is dissolved in hydrochloric acid, the solution nearly neutralised, tartaric acid is added, the mixture treated with hydrogen sulphide, then rendered ammoniacal, and filtered. After the filtrate has been acidified with sulphuric acid and boiled to expel hydrogen sulphide, the zirconium and titanium are precipitated together by "cupferron"; the titanium is estimated subsequently, either

colorimetrically or volumetrically, in the mixed oxides. [See further, *J. Soc. Chem. Ind.*, 1920, September.] W. P. S.

Immediate Analysis by Fractional Distillation, Method of Maxima and Minima. CHARLES MOUREU, CHARLES DUFRAISSE, and PAUL ROBIN (*Bull. Soc. chim.*, 1920, [iv], **27**, 523—527).—The method described, which is applicable to the separation of mixtures of substances with boiling points close together, consists of successive fractional distillations, the division into fractions being controlled, not by the boiling points, but by maximum or minimum values of physical properties, such as density, refractive index, viscosity, etc. The rectification is continued, similar fractions being united for further fractionation, until a fraction is obtained which, when subdivided by slow distillation, gives fractions all of which possess identical boiling points and physical properties.

A simple vaselin manometer is described by means of which very slight variations in pressure during distillation may be noted, and it allows of a distillation being interrupted and then very readily resumed at the same reduced pressure. W. G.

Critical Study of Methods for the Detection of Methyl Alcohol. ALEXANDER O. GETTLER (*J. Biol. Chem.*, 1920, **42**, 311—328).—Fifty-eight tests for the detection of methyl alcohol were critically studied to ascertain their trustworthiness, specificity, and sensitiveness, and the influence of foreign substances on them. They may be divided into two groups: (1) in which the methyl alcohol is oxidised to formaldehyde, which is then detected; (2) in which direct tests for methyl alcohol itself are applied. As oxidising agents for conversion of the methyl alcohol into formaldehyde, the author prefers alkaline permanganate or potassium dichromate and sulphuric acid. The colorimetric tests for the detection of formaldehyde which he considers most trustworthy are: with (1) phenylhydrazine + ferric chloride + hydrochloric acid (Meth, A., 1906, ii, 588); (2) phenylhydrazine + sodium nitroprusside + sodium hydroxide (Meth, *loc. cit.*); (3) *apo*morphine sulphate (Wolff, A., 1919, ii, 482); (4) peptone + ferric chloride + hydrochloric acid (Salkowski, A., 1919, ii, 249); (5) reduced magenta + sulphuric acid (Denigès, A., 1910, ii, 357, 461). These colour tests are extremely sensitive, 1 part in 200,000 being easily detected. Two confirmatory tests in which crystalline products are obtained are: (1) with β-naphthol + hydrochloric acid (Mulliken, "A method for the identification of pure organic compounds," 1911); (2) with concentrated ammonia, giving hexamethylenetetramine, which gives characteristic crystals with mercuric chloride (Romijn, A., 1896, ii, 280). These two tests require the presence of 5% of methyl alcohol.

All the methods, which are applied directly for methyl alcohol require a large amount of methyl alcohol. Of the twelve examined, the method of Leach and Lythgoe (A., 1905, ii, 655), is

which the relationship between specific gravity and refractive index is determined, is the most outstanding. As a colorimetric test, that described by Vivario (A., 1914, ii, 780), in which the alcohol is converted into potassium cyanide, is very good.

Details of the typical procedures for the detection of methyl alcohol in liquors and in tissues are given, and there is a full bibliography. W. G.

Diazometric Estimation of Phenol and of certain of its Homologues. Robert M. Chapin (*J. Ind. Eng. Chem.*, 1920, **12**, 568—570).—The method depends on the coupling of phenols with diazonium salts to form insoluble hydroxyazo-compounds. The reagent is prepared by mixing equal volumes of *N*/10-*p*-nitro-aniline solution and 1% sodium nitrite solution, and is standardised against β-naphthol. The phenol solution to be titrated is treated with 10% sodium acetate solution and basic lead acetate solution, and the reagent is added with constant stirring. Small, filtered portions of the mixture are tested from time to time with a drop of the reagent or a drop of phenol solution in order to ascertain the progress of the titration. [See, further, *J. Soc. Chem. Ind.*, 1920, September.] W. P. S.

Analysis of Phenolsulphonic Acids. Louis Desvergnes (*Ann. Chim. anal.*, 1920, [ii], **2**, 211—214).—About 5 grams of the sample are dissolved in water and diluted to 200 c.c. Ten c.c. of the solution are boiled for fifteen minutes with hydrochloric acid and bromine, diluted to 200 c.c., cooled, filtered, and the sulphuric acid is estimated in the filtrate as barium sulphate; this gives the total sulphuric acid (H_2SO_4) present. Ten c.c. of the solution are then titrated with *N*/2-sodium hydroxide solution, using methyl-orange as indicator; the combined sulphuric acid is calculated from the formula $(T-S)/2$, where T is the total sulphuric acid and S the sum of the total sulphuric acid and one-half of the combined sulphuric acid. The phenol is estimated by treating 10 c.c. of the solution with 100 c.c. of water and 50 c.c. of hydrochloric acid, adding a definite quantity of standardised potassium bromide–bromate solution, heating the mixture at 50° for thirty minutes in a closed vessel, and then titrating (iodometrically) the excess of bromine. Calculation gives the amount of free sulphuric acid present, and the proportion of phenol to combined sulphuric acid indicates the amounts of mono- and di-sulphonic acids in the sample. W. P. S.

Use of Potassium Ferrocyanide in the Analysis of Sugars by Alkaline Copper Solutions. E. Cordonnier (*Bull. Sci. Pharmacol.*, 1920, **27**, 137—138).—The use of potassium ferrocyanide, in the amounts indicated by its advocates, is capable of causing a complete reduction of Fehling's solution if the boiling is sufficiently prolonged. The method of Causse-Bonnans leads to

very serious errors if the conditions of heating are not accurately controlled. CHEMICAL ABSTRACTS.

Blood Sugar Concentration and Blood Sugar Methods. H. F. HÖST and ROLF HATLEHOL (*J. Biol. Chem.*, 1920, **42**, 347—358).—Bang and Hatlehol's method (compare A., 1918, ii, 279). and Hagedorn and Jensen's method (compare *Ugesk. Læger*, 1918, **80**, 1217), give in normal individuals and in diabetics values for the blood sugar concentration which agree approximately. The method of Folin and Wu (A., 1919, ii, 308), and particularly the modification by Myers and Bailey (A., 1916, i, 300) of Benedict's method, may, in the case of diabetics with hyperglycæmia, give results which are too high. W. G.

Method for the Estimation of Acetic Acid in Acetates. OSCAR A. PICKETT (*J. Ind. Eng. Chem.*, 1920, **12**, 570—571).—Xylene is used in place of water as a carrier for the acetic acid in the distillation of the acetate with phosphoric acid. About 350 c.c of xylene are used for 2·5 grams of the acetate, and the distillation is continued until only a thin film of xylene remains on the surface of the phosphoric acid solution in the distillation flask. W. P. S.

Degree of Alkalinity Necessary for the Phloroglucinol Test for Formaldehyde. PAUL J. HANZLIK (*J. Biol. Chem.* 1920, **42**, 411—413).—The degree of alkalinity necessary for a minimum positive reaction in the phloroglucinol test for formaldehyde is $P_H = 12·13$, or the equivalent of the alkalinity of $0·01N$-sodium hydroxide. For an optimum reaction, the alkalinity should be $P_H = 13·0$, or $0·1N$. W. G.

Estimation of Acetaldehyde in Paracetaldehyde. W STÜWE (*Apoth. Zeit.*, 1920, **35**. 153—154; from *Chem. Zentr* 1920, iv, 155).—Paracetaldehyde (5 c.c.) is brought into a 100 c.c flask and frequently shaken during a quarter of an hour wit $N/10$-mercuric chloride solution (10 c.c.), potassium iodide fr from iodate (2 grams), sodium hydroxide solution (15%, 20 grams and water (50 grams). The mixture is diluted to 100 c.c. ar filtered. Fifty c.c. of the filtrate are treated with gum arab (0·5 gram), sodium hydroxide solution (5 c.c.), and formaldehy (3 c.c.); after two minutes, the solution is acidified with dilu acetic acid (15 c.c.), and subsequently cooled. The precipitat mercury is dissolved by addition of a measured volume of $N/$ iodine solution, and excess of the latter is titrated. H. W.

Rapid Volumetric Methods for the Estimation of Ami acids, Organic Acids, and Organic Bases. FREDER WILLIAM FOREMAN (*Biochem. J.*, 1920, **14**, 451—473).—Ammo primary, secondary, and tertiary amines, and basic methylene de atives of secondary amines do not form ionisable compounds w phenolphthalein in aqueous-alcoholic solutions providing the c centration of alcohol is above 80%. In such solutions, theref

the acid radicles of the salts of these bases can be titrated accurately with $N/10$-potassium hydroxide, using phenolphthalein as indicator. Similarly, when aqueous-alcoholic solutions of certain amino-acids containing about 85% of alcohol are titrated with $N/10$-alcoholic potassium hydroxide, the amino- or imino-groups, liberated from their "internal salt" combinations, show no basicity to phenolphthalein, and the carboxyl groups are accurately estimated. Certain amino-acids, however, more particularly bibasic amino-acids and proline, give low results when titrated in alcohol under these conditions, possibly owing to loose combination of alcohol with a carboxyl group, or loose condensation, but a subsequent addition of formaldehyde or acetone results in a disturbance of the equilibrium, and then the carboxyl groups can be titrated quantitatively.

The guanidine nucleus of arginine behaves differently from other nitrogenous bases or basic groups in that it acts as a univalent base in both alcohol and water. Thus it is neutral to phenolphthalein in 85% alcohol solution, the carboxyl group and the guanidine nucleus exactly neutralising each other.

The complete estimation is carried out as follows: (1) Five c.c. of the aqueous solution are titrated with $N/10$-aqueous sodium hydroxide. (2) Ten volumes of 97% alcohol are added to 5 c.c. of the aqueous solution, and the mixture is titrated with $N/10$-alcoholic potassium hydroxide. (3) To the liquid from titration (2), 2·5 c.c. of neutral 13% aqueous formaldehyde solution are added for every 50 c.c. of alcohol present, and the titration continued to the same end-point. Titration (1) gives useful information when dibasic amino-acids, arginine, and salts of amino-acids are present. Titration (2) gives the correct estimation of a number of amino-acids. In titration (3), the carboxyl groups of all the amino-acids in an amino-acid mixture, except that of arginine, are estimated.

This new volumetric process forms a rapid and accurate method for use in the investigation of many important biochemical problems. For the estimation of volatile bases and amino-acids in "alcoholic extracts" (compare Foreman and Graham-Smith, *J. Hygiene*, 1917, **16**, 144), to an aliquot part of the extract the amount of alcoholic alkali necessary for neutralisation, as determined by titration (3), is added, and the mixture is distilled with steam free from carbon dioxide for about five minutes, the distillate being collected in standard acid. The excess of acid is titrated, using alizarin as indicator, and thus a measure of the volatile bases is obtained. The residual liquid in the distillation flask is free from alcohol, and, owing to the hydrolysis of the alkali salts of the amino-acids, is alkaline. It is titrated with $N/10$-acid, and thus a value is obtained for the amino-acids present in the original alcoholic extract." W. G.

Micro-estimation of Urea in Blood by means of Urease. . BAHLMANN (*Ned. Tydsch. Geneesk.*, 1920, **64**, [i], 473—478; from *Chem. Zentr.*, 1920, iv, 3—4).—The method of Cohen,

Fervaert, and Van Lier is modified in such a manner that the estimation can be made with 0·4 c.c. of blood. The ammonia, obtained by the action of the urease of the soja bean on the urea of the blood in faintly acid solution, is, after addition of alkali, drawn by a stream of air into very dilute hydrochloric acid, and excess of the latter is estimated iodometrically according to Bang's method. A blank experiment is performed with an equal quantity of blood without addition of urease. The amount of urea is calculated from the difference in the titrations in the two experiments. H. W.

Estimation of Hydrocyanic Acid in Beans. A. CZAPSKI (*Zeitsch. anal. Chem.*, 1920, **59**, 80).—Paraffin wax should not be used to prevent frothing of the contents of the distillation flask during the distillation of hydrocyanic acid from cyanogenetic beans; the wax inhibits partly the distillation of the acid, and less than one half of the amount of the latter actually present is found in the distillate. W. P. S.

Direct Estimation of Mercury Fulminate in the Mixtures for Detonators. M. D. MARQUEYROL (*Bull. Soc. chim.*, 1920, [iv], **27**, 448).—The mixture is extracted with a 5% solution of potassium cyanide, and the mercury is estimated by electrolysis in the extract. W. G.

A Pyrrole Reaction. E. SALKOWSKI (*Biochem. Zeitsch* 1920, **103**, 185—188).—The action of pyrrole on *p*-dimethylaminc benzaldehyde resembles that of indole, only it is less sensitive an is to a greater extent influenced by the addition of nitrite an fuming hydrochloric acid. The author points out the necessity ‹ taking this fact into consideration when carrying out Ehrlich reaction. S. S. Z.

Combination of Fractionation with Spectrophotomet in Proximate Organic Analysis. W. E. MATHEWSON (*J. Am Chem. Soc.*, 1920, **42**, 1277—1279).—The spectrophotomet method of estimating dyes may be applied to colourless orga compounds by first converting these into coloured compoun which are separated from the excess of reagents or other colou substances present by extraction with suitable solvents. Procedu are described for the estimation of sulphanilic acid, acetone, ‹ β-naphthol, depending on their condensation, respectiv with picryl chloride, 2:4-dinitrophenylhydrazine, and diazoti sulphanilic acid. J. K

Justification of the Sublimate-Ammonia Process for Estimation of Stercobilin. R. GOIFFON (*Compt. rend. Biol.*, 1920, **83**, 344—346; from *Chem. Zentr.*, 1920, ii, 755). reply to Borrien's objections (*this vol.*, ii, 520). E. H.]

The Extraction of Stercobilin. M. BRULÉ and H. GARBAN (*Compt. rend. Soc. Biol.*, 1920, **83**, 342—344; from *Chem. Zentr.*, 1920, ii, 754—755).—The extraction of stercobilin from excrement by solvents, such as amyl alcohol, chloroform, a mixture of chloroform and thymol, or 95% alcohol, is not complete. The extraction is better from acidified solutions, but under these conditions a change of the colouring matter appears to be brought about through oxidation. E. H. R.

Analysis of the Colouring Substances in Urine. I. The Division of Urine into Three Main Fractions as a Basis for the Analysis of its Colouring Substances. M. WEISS (*Biochem. Zeitsch.*, 1920, **102**, 228—246).—The urine is divided into three fractions. Fraction I consists of the red colouring substances—the urobilin fraction. Fraction II contains the yellow colouring substances—the urochrome fraction. Fraction III is composed of the colourless proteic acids—the histidine fraction. Fraction I, which is obtained by precipitating the urine with neutral lead acetate, and does not contain the urochrome, is responsible for about three-quarters of the coloration of the urine. Fraction II is precipitated from the filtrate of fraction I with 10% alkali hydroxide. Besides urochrome, this fraction contains urochromogen, which differs from urochrome by the fact that it gives the permanganate and diazo-reactions, reduces silver salts, and darkens more intensely on keeping, when a melanin group is eliminated, which the author considers to be a phenol derivative. The presence of urochromogen can be detected better in fraction II than in the original urine. The colourless fraction contains proteic acids. A tryptophan derivative is also present in the urine, which cannot always be identified with the chromogen of urorosein. S. S. Z.

Chemistry of the Proteins. E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1920, **102**, 89—98).—In order to obtain proteins free from adhering impurities, such as the products of protein degradation, fats, lipoids, etc., the clear extract from the tissues is precipitated with five to six volumes of 90% alcohol and heated on a boiling-water bath. It is then filtered or centrifuged, and the residue treated with boiling absolute alcohol, and again with boiling ether. The protein powder thus obtained is further extracted with boiling water to remove the albumoses, peptones, and salts. The authors also describe a method for the detection and estimation of the higher polypeptides in the protein solution. The protein and the higher polypeptides are precipitated with boiling 90% alcohol. The precipitated fraction is then extracted with boiling water, and the nitrogen is estimated in the aqueous extract. Using this method, it is found that all colloidal protein solutions contain appreciable quantities of albumoses. One hundred c.c. of human serum contain a quantity of albumoses and peptones equivalent to 0·4 gram of Witte's peptone. S. S. Z.

Rapid Estimation of Albumin in the Urine. L. Dupuy (*Presse medicale*, 1920, **28**, 104).—The turbidity of a standard solution of albumin is compared with that of the urine under examination after each has been treated with Eschlach's citric-picric acid reagent. Chemical Abstracts.

The Separation of Serum Proteins. M. Piettre and A. Vila (*Compt. rend.*, 1920, **170**, 1466—1468).—The serum is first neutralised by addition of *N*-hydrochloric acid. To it is added two and a-half times its volume of acetone. The precipitate is collected on a Buchner funnel, mixed with one volume of acetone, dried by suction, and washed with ether. The cake of proteins, without being broken up too much, is transferred to a dish, covered with water (70 c.c. for each 100 c.c. of serum originally taken), and left in contact with it for several hours. The water is then carefully decanted, and this process is repeated two or three times. Finally, the material is powdered and washed two or three times by centrifuging with water saturated with carbon dioxide. By this means, the insoluble proteins are obtained free from albumin. The washing waters are united, saturated with carbon dioxide, and filtered, and from the filtrate the albumin is precipitated by the addition of an equal volume of acetone.

In the aqueous-acetone liquors, the fats, lipoids, sugars, etc., can be estimated separately by the usual processes. W. G.

New and Improved Method for the Recognition of Human Blood. Angelo de Dominicis (*Boll. Chim. farm.*, 1920, **59**, 241—244).—A simple method for detecting human blood on a knife-blade or other non-absorbent surface consists in pouring on to the spot a very dense solution of celluloid in amyl acetate, allowing the solvent to evaporate, removing the dry pellicle by means of needles, and examining under the microscope the superficial layer of blood on the pellicle. If the latter cannot be removed from the blood-stained surface, it may be first thickened by a second application of the celluloid solution. T. H. P.

"Thiocol." C. A. Grau (*Bull. Sci. pharmacol.*, 1920, **27**, 17—22).—A diagram of the crystals formed by the reaction of thiocol with mercurous nitrate is given, together with the directions for making this microchemical test. As with guaiacol, so with thiocol, it is possible to test various plants for oxydases in the presence of hydrogen peroxide. The roots of artichoke, dahlia, chard, and lucerne are suitable materials responding positively to the test. Thiocol can also be used to demonstrate the presence of oxydase in the blood, and as a measure of renal insufficiency. Its use in the latter connexion depends on its detection in the urine by the rose colour developed when a few drops of the urine are placed on artichoke root, together with hydrogen peroxide. Its use is apparently incompatible with the presence of resorcinol, α-naphthol, and sodium salicylate. Chemical Abstracts.

General and Physical Chemistry.

Extension of the Balmer Series of Hydrogen and Spectroscopic Phenomena of Very Long Vacuum Tubes. R. W. Vood (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 455—470).—The author escribes a type of vacuum tube in which it is possible to separate he secondary spectrum of hydrogen from the Balmer series. The ube is 2 m. long and has a 7 mm. bore, and is bent so that the entral 40 cm. constitutes an "end on" tube, the electrodes of hich are 80 cm. away from the tube. The electrodes are of luminium; one end of the tube is in permanent connexion with Gaede pump and the other is connected by a fine capillary tube ith a hydrogen generator, either an electrolytic apparatus or a ulb containing palladium and hydrogen. The tube is operated at ,000 volts and 0·2 ampere. When the pressure is such that there is a Crookes dark space of 4—5 cm., the ends of the tube show a bluish-white light, whilst the central portion shows a fiery purple colour, which exhibits the Balmer spectrum with a secondary spectrum of 1/40th the intensity of that in the side-tubes. It is possible by finer adjustment that the secondary spectrum may vanish entirely. The failure to observe more than twelve members out of the thirty-two emitted by solar hydrogen in the Balmer series is attributed to the numerous lines in the secondary spectrum, which are relatively brighter than the Balmer lines. On photographing the spectrum of the central portion of the tube the author has been able to observe all the Balmer lines up to the 20th. In the region of the 6th to the 14th line each line is practically twice as bright as its succeeding neighbour. This means, if this rate of change is continued, that the 20th line has an intensity of about 1/600,000 that of the H_α-line. A number of other very interesting properties of the long tube are described. The following wave-lengths have been measured: 12th line, 3722·12; 13th, 3712·22; 14th, 3703·92; 15th, 3697·35; 16th, 3691·72; 17th, 3686·99; 18th, 3682·96; 19th, 3679·46; 20th, 3676·44, all with reference to Rowland's iron standards. The influence of water vapour on the appearance of the secondary spectrum is described. J. F. S.

Origin of "Cyanogen" Bands. S. Barratt (*Proc. Roy. Soc.*, 1920, [*A*], **98**, 40—49).—Observations have been made of the spectra of the flames of a number of gases containing carbon, hydrogen, nitrogen, and oxygen. The cyanogen bands are strongly developed in the coal gas–nitrous oxide flame. Evidence is obtained which shows that they are entirely absent from the hydrogen–nitrous oxide flame, if all traces of carbon are excluded, and it appears that carbon is essential to their production. The appearance of the cyanogen bands is, under appropriate conditions, a more delicate test for carbon than that of any other of the bands

associated with this element. On the other hand, this spectrum is not necessarily developed when both carbon and nitrogen are present. The conclusion of Grotrian and Runge, that the cyanogen spectrum is to be attributed to nitrogen, is shown to rest on assumptions which are not confirmed by the present work. The cyanogen spectrum provides a very delicate test for the presence of compounds of nitrogen admitted in the form of a gas to hydrocarbon flames burning in air, since elementary nitrogen does not appear, in ordinary circumstances, to be effective in producing cyanogen bands in such flames. The intensity of the cyanogen bands, when carbon compounds are admitted to the hydrogen-nitrous oxide flame, bears no simple relation to the amount of carbon thus added. J. F. S.

Character of the Light Radiations Emitted by the Vapours of Magnesium, Copper, and Manganese under the Selective Actions of Thermochemical and Thermoelectrical Excitations. G. A. Hemsalech (*Phil. Mag.*, 1920, vi, **40**, 296—315).—With an electrically heated plate of graphite, which is not covered with a layer of carborundum, the red fringe (this vol., ii, 1, 2, and 170) appears on both sides. The upper fringe often extends to a greater distance from the plate than the lower one, probably on account of convection of vapours expelled from the under surface. The border of the upper fringe is sharply defined and its spectrum emission stops abruptly, in marked contrast to that of the luminous vapour. In the absence of sufficient quantities of ionised vapours, strong magnetic fields (1500—2000 C.G.S.) must be applied to displace the red fringe emission appreciably, hence the conclusion previously advanced, that the sharp outline is caused by the magnetic effect of the heating current, is untenable. No satisfactory alternative explanation is offered, but it is pointed out that most luminous phenomena which owe their origin to the flow of an electric current at atmospheric pressure present a sharp outline.

The vapours which fill the protected space are in great part derived from substances on the plate, and the formation of striæ at the boundary surface is interpreted as due to motion of the vapours round the plate in a helical path. The downward drift of luminous vapour in the protected space may be due to gravity or radiation pressure, or their combined action.

An investigation of the spectrum lines emitted by the vapours of magnesium, copper, and manganese showed that the line emissions due to thermoelectrical and chemical excitation are of the same type. The characteristic flame lines of magnesium, copper, and manganese, which in the air-coal gas flame are emitted by the mantle above the cone, all appear as long lines in the single plate furnace. This confirms their status as temperature lines.

J. R. P.

The Fine Structure of the Near Infra-red Absorption Bands of Hydrogen Chloride, Bromide, and Fluoride. H. M. Randall and E. S. Imes (*Physical Rev.*, 1920, **15**, 152—155).—By

focussing on the slit of an infra-red grating spectrometer the spectrum produced by a prism spectrometer, using a salt prism of small refracting angle, the spectral region to be analysed is too short for the overlapping of spectra. It is possible to employ the full resolving power of a series of graded gratings with the result that in several instances the absorption curves show apparently complete resolution. The position of the narrow absorption bands can be determined with an accuracy of a few Å. In the case of the hydrogen chloride band at $3{\cdot}46\,\mu$, each member of the broad doublet was resolved into twelve narrow bands. From the data obtained, the moment of inertia of the molecules of hydrogen chloride, hydrogen bromide, and hydrogen fluoride is calculated as well as the distance between the atoms in the molecule.

CHEMICAL ABSTRACTS.

The Object and Possibility of an Analysis of Absorption Spectra. I. LIFSCHITZ (*Zeitsch. physikal. Chem.*, 1920, **95**, 1—14, 126. Compare this vol., ii, 208).—A theoretical paper, in which the object of absorption spectrum determination and the possibility of arranging absorption bands in some such series as are found for emission spectra are discussed. The reason for the latter is to remove absorption spectra from a purely empirical study and to find some connexion between the absorption bands and their arrangement and the chromophoric groups of the various substances. The term chromophore is redefined as follows. Chromophores are single atoms or groups of atoms which carry electrons capable of oscillation with frequencies between 0·3 and $1{\cdot}7\times10^{14}$. J. F. S.

Optical Effects Occasioned by Salt Formation with Organic Acids. I. Phenols and Enols. H. LEY (*Zeitsch. physikal. Chem.*, 1920, **94**, 405—442).—The absorption spectra of a number of phenols, phenolic substances, alcohols, and their sodium derivatives have been measured in alcoholic solution by the Hartley method, using an iron arc as the source of light. The following combinations in various concentrations have been measured and recorded: phenol, and sodium phenoxide in ethyl alcohol and in water; *p*-xylenol, *m*-4-xylenol, thymol, *p*-chlorophenol, *p*-bromophenol, ethyl 2-naphthol-3-carboxylate, *o*-, *m*- and *p*-hydroxycinnamic acids and their ethyl esters, melilotic acid and its ethyl ester, *p*-methoxystilbene, *p*-hydroxystilbene, 2-hydroxydiphenyl, benzoylacetic ester, β-ethoxycinnamic acid and its ethyl ester, and the sodium derivatives of all the compounds in ethyl-alcoholic solution. Absorption curves have been drawn in all cases, and the changes in the absorption spectra brought about by the salt formation pointed out and considered in the light of the present results and other previously published work. J. F. S.

Table for the Identification of Dyes by means of the Spectroscope. JAMES MOIR (*J. S. African Assoc. Anal. Chem.*, 1920, **3**, 9—13).—The position of the centre of the absorption band of a large number of dyes is given, ranging from that of Aurantia at λ 425 to that of tetramethylthionine at λ 668. W. P. S.

Colour and Chemical Constitution. IV. The Remaining Phthaleins. JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1919, 7 183—188. Compare A., 1917, ii, 349, 557).—Further wave-length measurements of absorption bands are communicated of a number of derivatives, several new, of *pp'*- and of *op'*-phenolphthaleins, and of 4'-hydroxydiphenylphthalide. Quantitative conclusions are derived as to the percentage increase in wave-length of the absorption band of phenolphthalein due to the introduction of various substituents In agreement with the view previously put forward as to the existence of secondary bands of the phthaleins with a wave-length two-thirds that of the visible band, phenolphthalein and thymolphthalein in alkaline solutions exhibit bands of which the edges are at λ 380 and λ 420 respectively. The centre of the band for *p*-cresolthymolphthalein in alkaline solution is at λ 595 whilst the value calculated from those for phenol-*p*-cresol- and phenolthymol-phthaleins is λ 597.

By condensation of 5-bromoguaiacol with hydroxybenzoylbenzoic acid, the bromine atom is eliminated and phenolguaiacolphthalein is produced. In this compound, therefore, and presumably also in guaiacolphthalein, it is the methoxy-group which occupies the para position to the central carbon atom (compare Hindmarsh, Knigh and Robinson, T., 1917, **111**, 941), and in dibromoguaiacol phthalein each bromine atom is in the ortho-position to the centra carbon atom and also to one hydroxyl group in each nucleus Quinonoid formulæ are suggested for the salts of quinolphthalein.

J. K.

Colour and Chemical Constitution. V. The Yellowness of certain Phthaleins when Acid. VI. The Ultra-violet Spectra of the Phthaleins. JAMES MOIR (*Trans. Roy. Soc S. Africa*, 1919, **8**, 41—44. Compare preceding abstract).—The absorption spectra of phenolsulphonephthalein, of benzaurin-*p*-sulphonic acid, and of phenolphthalein monomethyl ether (Green and King, A., 1907, i, 933) only differ from that of benzaurin in that the absorption band is moved slightly towards the red owing to the loading of the molecule with the sulphonic and carbomethoxy groups respectively. Further, since all three compounds are yellow in slightly acid solution whilst phenolphthalein is colourless under these conditions, it is concluded that phenolsulphonephthalein is not a phthalein but benzaurin-*o*-sulphonic acid.

Consideration of wave-length measurements by Howe and Gibson (*Physical Rev.*, 1917, 767) of the ultra-violet absorption band from alkaline solutions of phenolphthalein and its derivatives lead to a modification of the earlier formula (A., 1917, ii, 350) to $y=x-7$, indicating that in all phthaleins change of the grouping $:C{<}^{O^-}_{O^-}$ to $:C{<}^{OH}_{SO_4H}$ is accompanied by a diminution in frequency of 7 units.

J. K.

Colour and Chemical Constitution. VII. Spectra of Solid Compounds of Cobalt, Nickel, Manganese, and Uranium. JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1919, **8**, 45—49. Compare preceding abstracts).—Evidence is adduced to show that the effect on the absorption spectrum of loading the molecule either internally by substitution or by combination with a non-ionising solvent noted in the case of certain organic compounds may also be observed among cobalt, nickel, and uranyl salts and among permanganates. It is noted that the wave-lengths of homologous lines of cobalt compounds, of uranyl compounds, and of the phthaleins are respectively proportional to the eighth, sixth, and fourth roots of the molecular weights of the compouuds compared. J. K.

Colour and Chemical Constitution. IX. An Empirical Law of Change of Colour. JAMES MOIR (*Trans. Roy. Soc., S. Africa*, 1920, **8**, 225—228. Compare preceding abstracts).—An examination of the absorption spectra of the haloid derivatives of phenolphthalein and fluorescein has shown that the effect of the substituents on the position of the bands is given by the relation $\frac{n}{n_0}=1-\frac{m}{100}(1{\cdot}15+0{\cdot}0037N)$, in which n=the frequency for the halogen derivative, n_0 for that of the parent substance (18·05 for phenolphthalein and 20·27 for fluorescein), m=the number of substituent halogen atoms, and N=the atomic number of the halogen. The relationship also appears to hold approximately for alkyl derivatives. The view previously advanced that molecular volume is the main factor in colour change is abandoned in view of the fact that the introduction of methyl, *iso*propyl, chlorine, bromine, and iodine into the molecule produces about the same effect in each case. J. K.

Colour and Chemical Constitution. VIII. Fluorescence and its Laws. JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1919, **8**, 51—53. Compare preceding abstract).—The emission spectra of the green fluorescences exhibited by uranyl compounds in the solid condition or in non-aqueous solution have been examined. The bands are equally spaced and probably always five in nnmber, but usually some are too faint to be observed. It is found that for all of them $\frac{A_n}{A_l}=\left(\frac{F_n}{F_l}\right)^{\frac{4}{3}}$, in which A_n and F_n are corresponding wave-lengths in the absorption and fluorescent spectra, and A_l and F_l are the respective wave-lengths of the lowest bands in each. The relation also appears to hold for some organic compounds, which give much the same value, 1·15, for the ratio $\frac{A_n}{A_l}$. J. K.

Scattering of Light by Dust-free Liquids. W. H. MARTIN (*J. Physical Chem.*, 1920, **24**, 478—492).—Dust-free liquids were prepared (i) by evaporation and condensation in an enclosed

exhausted apparatus, (ii) by precipitating gelatinous hydroxides of aluminium, cadmium, and zinc from dilute solutions of the sulphates, and (iii) by cataphoresis of water. The dust-free liquids were all found to scatter light, that of short wave-length being scattered to a much greater extent than that of long wave-length. A relationship, $(\mu-1)^2/n$, formulated by Rayleigh and verified in the case of gases by Strutt, connecting the refractive index of the medium and its light-scattering power, showed some agreement in the case of the liquids investigated. The scattered light is very largely plane polarised in the case of liquids which scatter very little light, and the polarisation in different liquids decreases as the relative intensity of the scattered light increases. The polarisation is much less complete for liquids than for gases. Evidence is given to show that the phenomena observed are due to scattering and not to fluorescence. The following intensities of the scattered light are given in terms of that of toluene = 1 : water, 0·060; sulphur dioxide, 0·400; methyl alcohol, 0·160; ethyl alcohol, 0·180; ethyl ether, 0·236; ethyl acetate, 0·210; *iso*butyl chloride, 0·375; heptane, 0·374; *iso*butyl butyrate, 0·320; benzene, 0·91; toluene, 1·00; chlorobenzene, 1·52; ethyl benzoate, 1·55; and α-chloronaphthalene, 4·30.

J. F. S.

Re-examination of the Light Scattered by Gases in respect of Polarisation. I. Experiments on the Common Gases. LORD RAYLEIGH (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 435—450. Compare A., 1919, ii, 5).—An improved method by which the residual defect of polarisation in the light scattered by dust-free gases may be measured is described. This quantity has been ascertained for the commoner gases, and the following values of the intensity of weak component polarisation obtained: hydrogen, 3·83; nitrogen, 4·06; air, 5·0; oxygen, 9·4; carbon dioxide, 11·7; nitrous oxide, 15·4 (strong component = 100). The author is of the opinion that the error attached to these values is not greater than 5%, and is probably much less.

J. F. S.

Re-examination of the Light Scattered by Gases in respect of Polarisation. II. Experiments on Helium and Argon. LORD RAYLEIGH (*Proc. Roy. Soc.*, 1920, [*A*], **98**, 57—64. Compare preceding abstract).—The experiments previously described (*loc. cit.*) are continued for helium and argon. Since the scattering due to helium is so slight, special precautions were taken to ensure the purity of this gas, which consisted in allowing the gas to circulate through a layer of charcoal cooled by liquid air immediately before entering the experimental tube. The intensity of the weak component polarisation is found to be argon 0·46, helium $<6·5$ (strong component = 100). The total intensities of light scattered by helium and by air have been compared. The ratio found was 0·0170. Considering the difficulty of the experiment, this is considered to agree within the limit of error with the ratio of the squares of the refractivities, which is 0·0144.

J. F. S.

Influence of Ammonium Molybdate on the Rotatory Power of Malic Acid. E. DARMOIS (*Compt. rend.*, 1920, **171**, 348—350).—The rotatory power of solutions of malic acid is increased by the addition of ammonium molybdate (compare Gernez, A., 1889, 1147), and the values of α_D are found to increase at first with the weight of ammonium molybdate and then to become practically constant. If it is assumed that the acid and salt combine to form a compound and the values of $[\alpha]_D$ are calculated and plotted against the weight of ammonium molybdate added, the curve shows a steep rise to a maximum and then a rapid fall. A solution having the composition corresponding with this maximum, when evaporated, gave a crystalline *compound* having $[\alpha]$ $+219°$ for the yellow ray of mercury, and in addition a very sparingly soluble ammonium molybdate. W. G.

The Specific Rotation of Lævulose. WARREN C. VOSBURGH (*J. Amer. Chem. Soc.*, 1920, **42**, 1696—1704).—From measurements of the rotation of lævulose solutions at 25° the concentration varying from 2·6 to 20 grams per 100 c.c., the author deduces the formulæ $[\alpha]_D^{25} = -(88{\cdot}50 + 0{\cdot}145p)°$ or $[\alpha]_D^{25} = -(88{\cdot}50 + 0{\cdot}150c - 0{\cdot}00086c^2)°$, where p is the percentage by weight of the sugar in the solution and c the number of grams per 100 c.c. Over the temperature range 15—37° the variation of $[\alpha]_D$ with temperature is given by $[\alpha]_D^t = [\alpha]_D^{25} + (0{\cdot}566 + 0{\cdot}0028c)(t - 25)°$. The author considers that Ost's results (A., 1891, 1000) are best expressed by $[\alpha]_D^{20} = -(91{\cdot}50 + 0{\cdot}133p)°$.

For most purposes the values of $[\alpha]^t_{\lambda=546\mu\mu}$ are given by $1{\cdot}1809\,[\alpha]_D^t$, although the coefficient seems to vary very slightly with temperature and concentration. W. G.

An Apparatus for using in Photochemical Reactions the Luminous Energy Emitted by an Incandescent Lamp. V. VOLMAR and C. DUFRAISSE (*Bull. Soc. chim.*, 1920, [iv], **27**, 680—681).—A simple arrangement is described by means of which the necessary metallic filament lamp can be introduced into the reaction liquid contained in a glass vessel surrounded by a polished metal jacket, the whole being immersed in a bath by which the temperature can be controlled. W. G.

Experimental Decision of the Question of the Radioactivity of all Elements. G. HOFFMANN (*Ann. Physik*, 1920, [iv], **62**, 738—758).—A special very sensitive electroscope capable of photographic registration upon a chronograph and sensitive to 5000 ions per mm., or a deflection of 30 mm. per single α-particle, has been used to investigate the "natural" radioactivity of common materials. From the range of the α-particle it can be decided whether the radioactivity is due to known or new radio-elements. The range can be obtained by statistical methods from the observation of the ionisation produced by each α-particle for a large

number. A discussion of the results obtained for the natural ionisation of a hollow sphere of brass proves that it is not wholly due to radium and its derivatives or to thorium, but in large part to new α-rays of very short range from a very long-lived radio-element. The material emitted 0·108 α-particle per cm.^{2} per hour, with a maximum ionisation of 100,000, corresponding with a range of about 1·8 cm. at *N.T.P.* The period of the element producing it (? copper) must be at least $1·5 \times 10^6$ times that of uranium, and this agrees with the range found. F. S.

Reactions in Penetrating Radium Radiation and in Ultra-violet Radiation Filtered by Quartz Glass. ANTON KAILAN (*Zeitsch. physikal. Chem.*, 1920, **95**, 215—246).—Mixtures of fumaric and maleic acids containing respectively 24, 40, 48, and 64% of maleic acid have been subjected, in 1/50*N*-solutions for 2 to 3000 hours at 6—14°, to the radiation of 80—110 mg. of radium metal through 1 mm. of glass. On the assumption that the decrease in the titre of the solution (5—7%) is due to the formation of acrylic acid, it is found that in all cases but one the maleic acid concentration has increased. This follows from conductivity measurements on the radiated solutions. When the above assumption is approximately true the position of the equilibrium point is much the same when the solution has been radiated with either ultra-violet rays or with radium rays, namely, 72% at 45—50°. Neither by 1632 hours' radiation with the rays from 80 mg. of radium metal, nor by 48 hours' radiation from a quartz mercury lamp, is the density, the refractive index, or the velocity of change into ammonium cyanate, of a normal solution of urea, changed to an extent outside the experimental error. Between 25° and 37° the reaction velocity is increased fourfold for a temperature increase of 10°, which agrees with the measurements of Fawsitt at 90—99° (A., 1903, ii, 15). Similar treatment of aqueous solutions of formic acid changes neither the dissociation constant nor the amount of oxalic acid formation. Both types of radiation induce a decrease in the titre of the solutions, the rate of which decreases as the concentration increases. Only rays with a smaller wave-length than 0·34 μ are active. A similar treatment of aqueous solutions of benzoic acid produces reducing substances, formic acid and oxalic acid; the velocity of formation of these substances increases as the square of the concentration of the benzoic acid. In this case also only rays smaller than 0·34 μ are active. The time in which the same effects are brought about by radium rays and by ultra-violet light is in the case of formic acid 270:1 and benzoic acid 7:1.
J. F. S.

Colouring and Thermoluminescence of Glass produced by Radium Emanation. S. C. LIND (*J. physical Chem.*, 1920, **24**, 437—443).—A theoretical paper in which the colouring of glass and other materials by radium emanations is discussed. It is shown that all three types of ray have the same effect on the glass, and

that the colouring takes place when pure substances are exposed to the rays. The colour is discharged from both glass and quartz by heating at a temperature at which the former substance commences to soften. Violet glass is slowly decolorised by exposure to sunlight, whilst brown glass is changed to a bright yellow by sunlight or ultra-violet light. When a piece of violet glass is heated at temperatures below 200° in the dark it luminesces for a period which is longer the lower the temperature, and after it has ceased to luminesce a further exposure to the radiation is necessary before further luminescence is possible. In this process, however, the violet colour is not affected; the colour only disappears when the temperature is raised to about 500°, and there is no luminescence in the temperature interval 200—500°. The more recently the glass has been subjected to the radiation the lower is the temperature at which luminescence occurs; glass which has been recently exposed to radiation commences to luminesce well below the boiling point of water, whilst glass which has been kept for two to three years after exposure only luminesces at 200°.

J. F. S.

Solubility of Radium Emanation in Organic Liquids. ALFRED SCHULZE (*Zeitsch. physikal. Chem.*, 1920, **95**, 257—279).—The solubility of radium emanation has been determined in toluene, ethyl ether, chloroform, acetone, carbon disulphide, ethyl acetate, ethyl alcohol, hexane, water, aniline, and benzene at various temperatures with the object of testing Dolezalek's theory of gas solubility (A., 1910, ii, 184). The results show that this theory represents the experimental facts in a qualitative manner for the solubility of radium emanation, both in normal and associated solvents. As to the quantitative aspect of the case it is impossible to draw any conclusions because the amount of radium emanation dissolved is small, and measurements are thereby rendered very inexact. Despite this, it is possible to obtain trustworthy data of the solubility from measurements of the vapour tension of the emanation if the correct molecular weight of the solvent is brought into the calculations. On the other hand, it is possible to deduce directly, from the course of the solubility curve, trustworthy values of the molecular weight of the solvent and so gain an insight into the molecular condition of liquids.

J. F. S.

Geiger-Nuttall Equation. GERHARD KIRSCH (*Physikal. Zeitsch.*, 1920, **21**, 452—456).—Application is made of the hypothesis that the atomic nucleus consists exclusively of helium and hydrogen nuclei with electrons, and of the Geiger-Nuttall relation in the form given by Lindemann (A., 1915, ii, 720), to deduce regularities in the disintegration series of radium and thorium. From these regularities, applied to the actinium series, conclusions are formed as to the atomic weights of these elements. An attempt is also made to show that there are three radioactive disintegration series.

J. R. P.

α-Ray Rules. HANS TH. WOLFF (*Physikal. Zeitsch.*, 1920, **21**, 393—396).—The rule $\log R = x \log (K - s) + y$, where $\log R$ is the common logarithm of the range of the α-ray in cm. at *N.T.P.*, x a positive, and y a negative constant, K a constant, and s the order of the change in the disintegration series in which the α-particle is expelled, counting for the first $s = 0$, the second $s = 1$, and so on, represents the ranges of the α-rays of all four series approximately, the uranium series being considered two, from uranium-*I* to radium, and from radium emanation to radium-*C''*, polonium, actinium-*X*, actinium-*C*, and thorium-*C* being exceptions. The values of x and y change for each of the four series, and the value of K is one-fourth of the atomic weight for the thorium and first part of the uranium series, 58 and 60, and 54 and 55 for the second part of the uranium series and for actinium respectively.

Discussing this relation theoretically, by the aid of the quantum relation it is deduced that the α-particle is travelling in an orbit of radius ρ in the nucleus, given by the relation $\rho = (K - s)^{-x/3}$ const.

F. S.

Electron Affinity of the Sulphur Atom. M. BORN and ELIZABETH BORMANN (*Zeitsch. Physik*, 1920, i, 250—255).—*X*-Ray measurements of the crystal lattice of zinc sulphide and application of the lattice theory lead to the value of 50 for the electron affinity of the sulphur atom. This value corresponds with an ionisation potential of 2·16 volts. CHEMICAL ABSTRACTS.

Conductivity and Frequency. E. D. EASTMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 1648—1655).—It is suggested that the conductivity of solutions of electrolytes is smaller at zero frequency than at any frequency in a certain range immediately above zero. Measurements of *N*-potassium chloride and sulphuric acid of maximum conductivity are described, and it is shown that the difference between direct current conductivities and those at 1000 cycles does not exceed 0·02—0·03%, but the difference lies in the direction expected. The conductivity of *N*-potassium chloride at 25° given by Kohlrausch is confirmed within 0·1%. J. F. S.

The Thermoelectric Power of Pure Metals. H. PÉLABON (*Ann. Physique*, 1920, [ix], **13**, 169—187).—From a study of the variation of the thermoelectric power with temperature, at temperatures above the melting point of one metal of the couples, it is shown that the thermoelectric power of pure metals varies continuously with the temperature, there being no discontinuity at the melting point. For the metals in the liquid state the thermoelectric power is a linear function of the temperature, at least for lead, tin, and bismuth. For antimony the results are not so regular.

W. G.

Theory of Electrocapillarity. I. and II. ALEXANDER FRUMKIN (*Phil. Mag.*, 1920, [vi], **40**, 363—375, 375—385).—I. Gouy's theory

(A., 1917, ii, 291) that the superficial electric charge is zero at the maximum of the electrocapillary curve, but that there may be a potential difference between the mercury and the solution, due to adsorbed ions, is confirmed. The ordinary equation of the electrocapillary curve $\partial\gamma/\partial\psi = \epsilon$ is replaced by $\partial\gamma/\partial\psi = \epsilon + \Gamma_{Hg}F$, where γ = surface tension, ϵ = electric charge on unit surface of the mercury, ψ = potential difference between a decinormal calomel electrode and the mercury in the solution, Γ_{Hg} = adsorption excess of mercury in gm. equiv. per sq. cm. of dividing surface, F = 96,540 coulombs. The results are incompatible with Nernst's theory, based on electrolytic solution pressure, since the potential difference between solution and mercury is not necessarily connected with exchange of ions of mercury, but may be caused solely by adsorbed layers of anions and cations.

II. A modification of Gibbs's adsorption equation is deduced, in which separate account is taken of the adsorption of the anion and the cation, and is used to calculate the horizontal distance between the ascending and descending branches of electrocapillary curves at different concentrations (Gouy, *loc. cit.*). The results are in fair agreement with the observed values, but the calculation of the maximum is less satisfactory. J. R. P.

Activities of Ions in Aqueous Solutions of some Strong Electrolytes. FREDERICK H. GETMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 1556—1564. Compare Noyes and MacInnes, this vol., ii, 345).—The *E.M.F.* of cells of the type Hg,HgCl | $MCl(c_1)$ ‖ $MCl(c_2)$ | HgCl,Hg, in which M is sodium, potassium, or hydrogen, and in which the concentrations varied over wide limits, have been measured at 25°. In addition, the two cells Hg,HgCl | 0·1*N*KCl ‖ 0·1*N*NaCl | HgCl,Hg and Hg,HgCl | 0·1*N*KCl ‖ 0·1*N*HCl | HgCl,Hg have also been carefully measured, and from the results the activities of the ions have been calculated. The results show, as in the work of Beattie and MacInnes (this vol., ii, 467), that the conductivity–viscosity ratio does not afford a trustworthy measure of the activity of the ions of strong electrolytes. Furthermore, the marked increase in the activity-coefficient of hydrochloric acid, which occurs beyond 0·5*N*, proves conclusively that this quantity cannot be proportional to the degree of ionisation. J. F. S.

Electromotive Behaviour of Aluminium. I. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 876—881).—A theoretical paper in which an explanation of the valve action of aluminium is put forward. The ennobling of the aluminium potential on anodic polarisation occurs as follows. During the withdrawal of electrons from the metal, represented by $3\theta_S$, aluminium ions pass into solution, $Al_S^{\cdots} \longrightarrow Al_L^{\cdots}$, and because this heterogeneous equilibrium is established instantaneously the reaction $Al_S \longrightarrow Al_S^{\cdots} + 3\theta_S$ proceeds with a very small velocity, so that the metal becomes poorer in ions and electrons. In consequence of this the potential of the metal becomes more positive, as is seen from the

equation $E=0{\cdot}058/\nu \cdot \log L_M/M^{\nu}_{L} - 2{\cdot}8$, because in this case L_M becomes smaller. Since the metal is inert the discharge potential of oxygen will soon be reached and oxygen will be liberated, which in certain circumstances may lead to the formation of an adherent coating of oxide on the metal. This coating gives rise to a certain resistance which may rise to a considerable value with increasing thickness. The assumption, however, that the resistance of such a coating should be different for different directions of the current is not justifiable, so that the sudden decrease of resistance on reversal of the current must be due to another cause. The small quantity of oxygen absorbed by the metal is a negative catalyst towards the setting up of the internal metal equilibrium. Hence the metal surface, being very poor in ions and electrons, passes into a metalloid condition, that is, it possesses small conductivity. Hence on anodic disturbance the aluminium surface becomes a metal layer of great resistance, and this coating is in turn surrounded by another of alumina. On reversal of the current the hydrogen liberated removes the absorbed oxygen, and the aluminium surface is transformed with great velocity into a condition of internal equilibrium, that is, the coating of great resistance is changed into one of negligible resistance. Hence the resistance remaining when aluminium is changed from anode to cathode is chiefly the resistance of the alumina. J. F. S.

Ignition of Gases at Reduced Pressures by Impulsive Electric Sparks. W. M. THORNTON (*Phil. Mag.*, 1920, vi, **40**, 345—356).—Ignition by impulsive sparks is, on the whole, more difficult at low pressures, in this differing from ignition by hot wires In hydrogen and methane the increase of difficulty takes place b well-marked steps or stages. In ethane or propane this does no occur, but there is an oscillation of the curve, found also in hydr gen and carbon monoxide. This appears to be associated with th temperature of the sparking point during the passage of the spark It has been shown previously (A., 1914, ii, 524, 834; 1915, ii, 734 that at pressures well above atmospheric sudden changes of inflam mability occur when ignition is by impulsive sparks or condense discharge. It is now found that there are such steps at reduce pressures, and that there is a close agreement between the parti pressures corresponding with the points at which oxygen has rati to the mass of the combustible gas expressed by successive natur numbers, and the pressures at which sudden changes of inflamm bility occur. J. R. P.

Dye Cells. E. STAECHELIN (*Zeitsch. physikal. Chem* 1920, **94**, 542—591).—The change in *E.M.F.* produced in cel containing various fluorescent dyes on illumination with a 30 candle-power half-watt lamp has been measured against *N*-calomel electrode. Rhodamine-*B*, rhodamine-3*B*, sodium eosi quinine sulphate, tetrachlorofluorescein, the phosphine dye, t sodium salts of *β*-naphthylamine-6:8- and 5:7-disulphonic aci

ıd resorufin, were all measured both alone in solution and in the resence of oxidising and reducing agents, such as acetaldehyde, ›rmaldehyde, oxalic acid, ferrous sulphate, iodine, vanadium ›troxide in sulphuric acid, ferric sulphate, hydrogen, oxygen, uinol, and other substances, such as potassium chloride, iodide, ıd sodium carbonate. It is shown that the Becquerel effect takes lace in both directions, and its dimensions and direction depend ı the presence of reducing and oxidising agents. The behaviour f all the cells examined can be explained by the assumption of a idden oxygen-hydrogen photolysis. J. F. S.

Metastability of the International Weston Element and s Unsuitability as an [Electrical] Tension Normal. ERNST OHEN and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1920, 5, 285—304).—The international Weston element with a 12·5% ıdmium amalgam, which was recommended by the international ›nference on electrical standards and units (Washington, 1908), oes not fulfil the demands which are required from a standard of lectromotive force. This is because the results of Cohen (A., 1900, , 702), Bijl (A., 1903, ii, 6), and F. E. Smith (*Collected Researches at. Phys. Lab.*, 1910, **6**, 137) on the composition of the element ave not been sufficiently taken into account. This element at temeratures below 12° is a metastable system, which may spontaneusly become stable with a noticeable change in the *E.M.F.* amountıg to about 6 millivolts at 0°, and for this reason is unsuitable as a ·andard. The temperature formula recommended by the confernce for use between 0° and 40° with this element refers to elements hich are metastable up to 12° and stable above this temperature. he Weston element is to be replaced by an element containing 8% ıdmium amalgam as recommended by Cohen and Kruyt (A., 1910, , 178, 259), which is stable from a few degrees below zero to 40°. he temperature formula mentioned above is strictly applicable to lements containing 8% cadmium amalgam from 0° to 40°, and ıay be applied to all such elements which are stable over this range f temperature. The Weston elements supplied by the Weston ompany containing 12—13% cadmium amalgam are also unstable elow 12°, and are also unsuitable as normals of electromotive force. J. F. S.

Moving Striations in Neon and Helium. F. W. ASTON nd T. KIKUCHI (*Proc. Roy. Soc.*, 1920, [*A*], **98**, 50—56).—When he flash of an ordinary spectrum tube containing neon or helium analysed by a rotating mirror it is found to consist of an xtremely short flash followed by a flame or arc, and that the latter onsists of bright striations travelling from anode to cathode. The elocity of these striations is found to be about 50,000 cm./sec. in eon and 100,000 cm./sec in helium. These values are a limiting ase, and the velocity varies with varying conditions, such as presure, diameter of tube, and temperature. Neither air nor hydrogen

showed moving striations in capillary tubes, but in a tube 1·6 mm. wide both developed stationary striations at 1 mm. to 2 mm. pressure. J. F. S.

Variation of Magnetic Susceptibility during Allotropic Transformations and Melting of some Substances. TORAJIRÔ ISHIWARA (*Sci. Rep. Tohoku Imp. Univ.*, 1920, **9**, 233—241).—The magnetic susceptibility of five weakly magnetisable substances was examined over considerable ranges of temperature in a modified torsion balance apparatus which could be exhausted or filled with inactive gas. Water was used as the standardising substance of the apparatus, its specific susceptibility being accurately known. Silver bromide is diamagnetic. On cooling, its susceptibility is fairly constant down to 200°, below which there is a slight decrease but no discontinuity in passing through the melting point. Silver chloride is also diamagnetic, the susceptibility increasing with rising temperature, with no discontinuity during fusion. The diamagnetic susceptibility of sulphur shows no discontinuity at the transformation from rhombic into monoclinic crystals, and the curves give no definite indication of fusion, but the transformation in the liquid phase at 160—170° is accompanied by a decrease of about 2% in diamagnetism, after which the susceptibility is again constant. There are indications of a reversible magnetic change at about 80° which may be due to the presence of an amorphous sulphur. The diamagnetic susceptibility of zinc shows a sudden decrease of about 4% at the melting point with a linear decrease above and below this point. Aluminium is paramagnetic, and its susceptibility is constant over a range of 100° below its melting point. During fusion it increases by about 2% and then remains constant.

T. H. B.

Molecular Theory of the Paramagnetism of Solid Salts. OTTO STERN (*Zeitsch. Physik.*, 1920, i, 147—153; from *Chem. Zentr.*, 1920, iii, 297).—Curie's law, xT=const. (where x is the susceptibility and T the absolute temperature), has been applied by Weiss to solid substances on the basis of Langevin's theory and on the assumption that here also the molecules, as carriers of the elementary magnets, are able to rotate freely. Since, however, doubts have been cast on this assumption, Weiss endeavoured to show later that it is not really essential if the condition is fulfilled that the molecules are attached to stable equilibrium positions or, in consequence of temperature changes, oscillate round these positions, provided only that the orientation of these equilibrium positions does not occur in any preferential direction (amorphous substances and crystalline powders). The detection of an error in Weiss' calculations has led the author to recalculate the entire subject. He is led to the diametrically opposite conclusion that the susceptibility of such a substance is independent of the temperature to a first approximation, and only as a second approximation decreases somewhat but only very slightly with increasing tempera-

ture—a result which could be predicted without calculation. Curie's law cannot therefore be valid for molecules oscillating round an equilibrium position, but only for such as are able to rotate freely. Since the molecules in a crystal certainly do not conform to this condition and Curie's law is known to be valid, the author is led to the conclusion that the molecules cannot be regarded as the carriers of the magnetic moment, and that this function is probably performed by the ions. H. W.

Volume Change Produced on Diluting Concentrated Solutions or Mixing Two Liquids. [FRL.] IRENE D. GÖTZ (*Zeitsch. physikal. Chem.*, 1920, **94**, 181—209).—The thermal expansion of ethylene dichloride, benzene and ethyl ether under a pressure of 420 and 350 atms. respectively has been determined over the range 0—40°; the volume change is represented by the following equations: ethylene dichloride, $v=0·78025(1+0·0011109t+0·000001696t^2)$; ethyl ether, $v=1·35786(1+0·0015006t+0·0000437t^2)$; benzene, $v=1·11250(1+0·0011715t+0·000000155t^2)$. The thermal expansion of mixtures of ethyl ether–ethylene dichloride and ethyl ether–benzene of various concentrations has been determined and found to be the same as that of ethyl ether under definite external pressure. These pressures were proportional to the concentration of the ethylene dichloride up to 49·875% and to that of the benzene up to 100%. Making use of Tammann's law of concentrated solutions, the contraction on mixing a concentrated solution of ethylene dichloride in ethyl ether with ethyl ether has been calculated and the values found to be very near the experimentally determined value. The contraction on mixing ethyl ether with benzene has been calculated on the assumption that two liquids only differ from one another and from their mixture in respect of their internal pressure, and the volume change depends only on the total pressure. The calculated values are very nearly those determined experimentally, except in a few cases.

J. F. S.

Graphic Representation of the Characteristic Equation. R. MOLLIER (*Physikal. Zeitsch.*, 1920, **21**, 457—463).—The magnitude $y=pv^2/T$ is plotted as ordinate against the density or the reciprocal of the absolute temperature as abscissæ. The resulting diagrams for different characteristic equations are discussed.

J. R. P.

Theory of the Solid State of Aggregation. A. VAN DER WERTH (*Zeitsch. physikal. Chem.*, 1920, **95**, 129—138).—A theoretical paper in which a number of properties of solids are treated mathematically. It is shown that the specific heat and the mechanical solidity bear a simple relationship to one another. Both quantities depend on the molecular attraction, and furnish a measure of the resistance with which a substance opposes any force which tends to disrupt it. This resistance is termed the "work of expan-

sion," and may be calculated from the modulus of elasticity and also from the specific heat and the thermal expansion. The following relative values have been calculated for the lengthening by 1/100 mm. of the following substances, from the specific heat values: Al, 8·05; Pb, 5·2; Cd, 8·07; Fe, 31·25; Au, 18·08; Cu, 20·37; Na, 0·168; Ni, 29·7; Pd, 24·45; Pt, 32·7; Ag, 12·7; Bi, 9·41; Zn, 9·67; and Sn, 7·1. The values calculated from the modulus of elasticity in many cases differ very much from the above values. The method adopted in the above calculations permits of qualitative conclusions being drawn in connexion with the mechanical properties of solid substances from simple thermal data.

J. F. S.

An Electrical Adiabatic Calorimeter and its Use in the Determination of the Specific Heat of Solutions of Cadmium Sulphate. Ernst Cohen and A. L. Th. Moesveld (*Zeitsch. physikal. Chem.*, 1920, **95**, 305—327).—The construction of an adiabatic calorimeter is described, which in its chief points follows closely the adiabatic calorimeter of Richards (A., 1908, ii, 806). The main point of difference lies in the heating of the liquid in the protecting jacket. Richards changed the temperature of the jacket by neutralising sodium hydroxide solution at a measured rate, whilst in the present case the change in temperature is effected by the passage of a known amount of electrical energy into the water in the surrounding jacket. An accuracy of 0·5 per 1000 is claimed for the results obtained with this instrument. The specific heat of solutions of cadmium sulphate from 1·89% to 44·63% (by weight) has been determined, and values obtained which steadily fall from 0·9763 with the most dilute solution to 0·5725 with the most concentrated. The results are compared with the values obtained by Berthelot-Thomsen and found to differ by quantities varying from 1/7000 to 36/6000.

J. F. S.

Indirect Method of Determining the Specific Heat of Dilute Solutions with Preliminary Data Concerning Hydrochloric Acid. Theodore W. Richards and Allan W. Rowe (*J. Amer. Chem. Soc.*, 1920, **42**, 1621—1635).—The specific heat of a dilute solution can be determined indirectly from the difference in the heat developed on diluting a known concentrated solution to a solution of the desired strength at two temperatures. The method is based on Kirchhoff's law, $K_w - K'_w = (U' - U)/\Delta\theta$, in which K_w and K'_w are the molecular heat capacities of the two substances, U and U' the respective total energy changes, that is, the heats of dilution at θ and $(\theta + \Delta\theta)$. This method has been carried out with the uttermost care for solutions of hydrochloric acid. The following molecular heats of dilution have been obtained for 20°: $HCl,10H_2O + 15H_2O$, 714 cal.; $HCl,10H_2O + 40H_2O$, 949; $HCl,10H_2O + 90H_2O$ 1082; $HCl,20H_2O + 80H_2O$, 480; $HCl,10H_2O + 190H_2O$, 1161 $HCl,20H_2O + 180H_2O$, 549; $HCl,10H_2O + 390H_2O$, 1219 $HCl,10H_2O + 790H_2O$, 1247. The following specific heats, for which

an accuracy of about 0·05% is claimed, have been obtained: $HCl,10H_2O$, 0·752; $HCl,20H_2O$, 0·849; $HCl,25H_2O$, 0·8776; $HCl,50H_2O$, 0·9320; $HCl,100H_2O$, 0·9634; $HCl,200H_2O$, 0·9812; and $HCl,400H_2O$, 0·9905. This method of determining specific heats is to be recommended because it is easier to measure two heats of dilution than one direct specific heat. J. F. S.

Variation of the Specific Heat of a Gas with Temperature. GEORGE W. TODD (*Phil. Mag.*, 1920, [vi], **40**, 357—362).—It is shown that continuous change of specific heat with temperature is not inconsistent with the theory of equipartition, and that the data for hydrogen are explained by the theory of equipartition as well as by the quantum hypothesis. It is assumed that gas molecules have three degrees of freedom so long as their velocities are below a critical value; above this value collisions result in the acquisition of further degrees of freedom. J. R. P.

Specific Heat of Saturated Vapours at Low Temperatures. E. ARIÈS (*Compt. rend.*, 1920, **171**, 456—458).—A criticism of Bruhat's work (this vol., ii, 528), in which the author reaffirms his own views on the subject (A., 1917, ii, 192). W. G.

Third Law of Thermodynamics and the Entropy of Solutions and of Liquids. GILBERT N. LEWIS and G. E. GIBSON (*J. Amer. Chem. Soc.*, 1920, **42**, 1529—1533).—A theoretical paper in which the Nernst third law of thermodynamics and the entropy of liquids and solutions are considered. The third law of thermodynamics is restated as follows: "If the entropy of each element in some crystalline form is taken as zero at the absolute zero, the entropy of any pure crystal at the absolute zero is zero and the entropy of any other substance is greater than zero." It is, however, likely that the difference between the entropy of a pure substance in the crystalline state and in any amorphous state may, in many cases, prove to be very small. J. F. S.

Entropy Changes at Low Temperatures. I. Formic Acid and Carbamide. A Test of the Third Law of Thermodynamics. G. E. GIBSON, W. M. LATIMER, and G. S. PARKS (*J. Amer. Chem. Soc.*, 1920, **42**, 1533—1542).—The specific heat of formic acid and of carbamide has been determined at a large number of temperatures from 71·0° *K* to 300·3° *K*. For formic acid the following values have been obtained: 71·0° *K*, C_p per gram = 0·157; 90·3° *K*, C_p = 0·182; 250·5° *K*, C_p = 0·344; and 291·5° *K*, 0·510; for carbamide the results include: 86·4° *K*, C_p = 0·239; 107·5° *K*, C_p = 0·259; 244·2° *K*, C_p = 0·382; and 300·3° *K*, C_p = 0·460. From these values the free energy and entropy have been calculated, and the following values, which are in keeping with the third law of thermodynamics (see preceding abstract), are obtained: Formic acid, $S_{p281·5°}$ = 4·72 per atom, and $S_{p281·5°}$ = 4·86 per atom or 24·30 per mol.; the entropy of fusion is 8·60.

S_{298°(liquid) = 34·2. The free energy of formation from the elements is −85370 cal., and from carbon monoxide and water 3415 cal., both at 298° *K*. Carbamide, S_{298° = 41·0 ± 2·0, and the free energy of formation from the elements is ΔF_{298° = −48,992 cal. J. F. S.

Entropy Changes at Low Temperatures. II. Ethyl and Propyl Alcohols and their Equimolecular Mixture. G. E. GIBSON, G. S. PARKS, and W. M. LATIMER (*J. Amer. Chem. Soc.*, 1920, **42**, 1542—1550. Compare preceding abstract).—The specific heat of ethyl alcohol, propyl alcohol, and an equimolecular mixture of the two has been determined for the liquids, crystalline solids, and the glasses at temperatures from 78·5° *K* to 274·6° *K*. The heat of fusion of ethyl alcohol at the melting point 156·2° *K* is found to be 24·0 cal. per gram or 123 cal. per gram-atom. The molecular heat capacities are: ethyl alcohol, 268·7° *K*, 24·39; 198·3° *K*, 21·10; 90·0° *K*, 12·80; and 86·0° *K*, 12·15; propyl alcohol, 268·7° *K*, 30·96; 198·3° *K*, 26·67; 90·0° *K*, 15·17; and 86·0° *K*, 14·47, whilst the values for the equimolecular mixture at the same temperatures are 27·72, 23·83, 13·90, and 13·21 respectively. From the data it appears probable that the entropy of the equimolecular mixture is not zero at the absolute zero. Assuming the validity of the third law of thermodynamics to the process ethyl alcohol (supercooled) ⟶ ethyl alcohol (crystalline) $\Delta S_{156\cdot 2}$, has been calculated by two methods. The difference (per gram-atom) between the results obtained is 0·12 cal. per degree or 20 cal. at 156·2° *K*. By means of the third law of thermodynamics the free energy of ethyl alcohol has been calculated to F_{298° = −43,000 cal. J. F. S.

Space-filling and Ionic Mobility. RICHARD LORENZ (*Zeitsch. Elektrochem.*, 1920, **26**, 383—384).—The author refers to the work of H. Kauffmann (this vol., ii, 16) as of importance in the extrapolation of electric conductivities to the limiting value, but differs from him in considering the boiling points as corresponding states for liquids. J. R. P.

Some Little-noted Sources of Error in Boiling-point Determinations under Reduced Pressure. C. VON RECHENBERG and E. BRAUER (*Zeitsch. physikal. Chem.*, 1920, **95**, 184—214).—A large number of experiments on the determination of boiling points under reduced pressure are described. It is shown that the temperature of the vapour in the boiling tube decreases from the bottom upwards, in individual cases as much as 20°. The electrically determined temperature measurements of Hansen (A., 1910, ii, 827) show that there is a more rapid fall of temperature between the surface of the boiling liquid and a height 1—2 cm. above it than elsewhere, which may be explained by the presence of fine drops of superheated liquid carried upward by the vapour. The temperature gradient in the upper half of the boiling tube is regular, and occasionally greater than in the lower half. The temperature fall therefore increases from the bottom upward, and this is true in all cases

and with all variations of heating and temperature of the mantle. With increase in the heating, that is, with increase in the amount of vapour evolved, the temperature increases at all points in the boiling tube, but in general the temperature gradients and temperature differences do not change to any marked extent. The temperature of the surrounding mantle influences the temperature of the vapour to a marked extent. The following conditions are recommended for the determination of boiling points by the dynamic method. The boiling flask may be of glass or metal; in the latter case a flattened bottom is preferable, whilst in the case of glass a second neck carrying a capillary tube is advantageous. The neck of the flask should be surrounded with a vapour mantle; the boiling tube must be at least 20 mm. wide, the neck and condenser tubes 15 mm. wide. The thermometer bulb must be placed at least 50 mm. above the level of the boiling liquid and the whole of the mercury thread should be in the vapour. Pressure measurements should be made on the boiling tube. The manometer should have a limb 15 mm. wide and must be perfectly vertical, and pressures of less than 5 mm. should not be measured in this way. The velocity of distillation must never be greater than one drop per second, and no temperature or pressure readings should be made until at least 10 c.c. have distilled over. J. F. S.

The Boiling Points, Critical Temperatures and Pressures in Homologous Series. MAURICE PRUD'HOMME (*J. Chim. physique*, 1920, **18**, 94—102).—In a homologous series the value of T_1/T_c increases from one member to the next higher in the series, T_1 being the absolute boiling point and T_c the absolute critical temperature. (T_c-T_1) increases or decreases similarly according to the particular series, and T_1/T_c divided or multiplied by (T_c-T_1) is a constant for each series.

The difference in the critical temperatures of two adjacent members in the series of paraffin hydrocarbons is given by $\Delta=210/T_c^{0\cdot0135T\sqrt{T_c}}$.

For isomeric esters, $(T_c-T_1)/(T_c-T_2)$ is a constant, where T_1 and T_2 are the absolute boiling points at two different pressures. Further, (T_c-T_1) is an exponential function of the critical pressure.

The introduction of any one of the halogen elements into a hydrocarbon gives for T_1/T_c and $T_c/(T_c-T_1)$ constant values independent of the nature of the halogen. W. G.

Ulrich Dühring's Law of Boiling Points at Similar Pressures. The Zero Point of Vaporisation. C. VON RECHENBERG (*Zeitsch. physikal. Chem.*, 1920, **95**, 154—183).—A theoretical paper in which Dühring's rule is examined by means of a large amount of previously published vapour pressure data. It is shown that this rule may be restated as follows. The saturation temperatures, for equal pressures of pure uniform chemical substances having similar vapour-pressure curves, change in the same way if the compounds during vaporisation do not change their

constitution, that is, neither dissociate nor associate, and when the vapour is entirely unimolecular. The author postulates a minimum temperature at which a substance ceases to exert a vapour pressure; this is the temperature at which vapour ceases to be capable of existence, and is termed the zero of vaporisation; it differs for every substance, and if it is found experimentally for a single substance can be calculated for all others by Dühring's rule. The vaporisation zero of hydrogen is the same as the absolute zero, as follows from the vapour-pressure determinations of Travers, Senter, and Jaquerod (A., 1903, ii, 9). Using this value, those of about fifty other substances have been calculated. The values of the more common substances are: oxygen, −243·91°; carbon dioxide, −171·49°; ammonia, −161·83°; chlorine, −182·29°; ethyl ether, −146·73°; ethyl alcohol, −91·96°; benzene, −129·71°; water, −87·84°; benzoic acid, +1·73°; glycerol, +27·85°; and sulphur, 6·57°. J. F. S.

Vapour Pressure Equation. CYRIL H. MEYERS (*Phil. Mag.*, 1920, [vi], **40**, 362—363).—The equation of Todd and Owen (A., 1919, ii, 495) is criticised adversely. J. R. P.

Approximation Formulæ for Univariant Systems. J. A. VAN LIEMPT (*Zeitsch. anorg. Chem.*, 1920, **111**, 280—288).—A theoretical paper in which the author deduces formulæ by which the vapour pressure and sublimation pressure in univariant systems may be approximated from known data. The formulæ are based on the Clapeyron formula, $dp/dT = Q_v/(v_g - v_e)T$, and have the form $\pi = -0{\cdot}2184k_1T_k\tau + 0{\cdot}2184k_1$, in which k_1 is the Trouton constant (21), T_k the boiling point, and $\tau = 1/T$, the temperature under discussion; supplying the value of the constants, the formula becomes $\pi = -4{\cdot}59T_k\tau + 4{\cdot}59$. This formula holds in the region of the critical point if it is written in the form $\log p_{crit} = -4{\cdot}59T_k/T_{crit.} + 4{\cdot}59$ The sublimation pressure is given by $\pi = -(2{\cdot}95T_s + 4{\cdot}59T_k)\tau + 7{\cdot}53$. J. F. S.

Liquefaction of Air and the Characteristic Equation. K. SCHREBER (*Physikal. Zeitsch.*, 1920, **21**, 430—433).—A discussion of the Joule-Kelvin effect leads to the characteristic equation $v^3 - (RT/p - a/T + c)v^2 - bR^2T = 0$, instead of van der Waals's equation $v^3 - (RT/p + b)v^2 - av/p + ab/p = 0$. J. R. P.

Heat of Reaction. WALTHER JANKOWSKY (*Zeitsch. Elektrochem.*, 1920, **26**, 385—391).—The energy-content of a body consists of heat and potential energy, which are interconvertible. Nernst's theorem is deduced from this assumption. Kirchhoff's equation for the dependence of heat of reaction on temperature, and Nernst's use of the equation, are said to be incorrect. The author believes that affinity is independent of temperature. J. R. P.

Heats of Combustion of Benzene, Toluene, Aliphatic Alcohols, *cyclo*Hexanol, and other Carbon Compounds. THEODORE W. RICHARDS and HAROLD S. DAVIS (*J. Amer. Chem. Soc.*, 1920, **42**, 1599—1617).—The heat of combustion of a number of carbon compounds has been most carefully determined, and the following values obtained in 18° calories per gram: sucrose, 3943; benzoic acid, 6320; naphthalene, 9614; benzene, 10,014; toluene, 10,155; *tert.*-butylbenzene, 10,434; *cyclo*hexanol, 8882; di*iso*amyl, 11,339; methyl alcohol, 5326; ethyl alcohol, 7101; propyl alcohol, 8033; *n*-butyl alcohol, 8615; and *iso*butyl alcohol, 8599. The heat effect for the addition of CH_2 in alcohols, and in the side-chains of aromatic hydrocarbons, is 648 kilojoules or 153·5 Cal., whilst that for the addition of CH_2 in the benzene ring is 638 kilojoules.

J. F. S.

Calculation of Theoretical Heats of Solution. H. VON STEINWEHR (*Zeitsch. physikal. Chem.*, 1920, **94**, 6—24).—A theoretical paper in which the calculation of the theoretical or fictitious heat of solution is considered. It is shown that the two most important methods for calculating this quantity, as put forward by Cohen and Bruins (A., 1918, ii, 297), are only possible in the case of anhydrous salts. The method applicable to hydrates, which can also be applied to anhydrous salts, was deduced by W. Jaeger (*Ber. Deut. physikal. Ges.*, 1901, **3**, 48), and has now been developed without the objections which were raised to Jaeger's method, and it has been used to calculate the fictitious heat of solution of $CdSO_4,8/3H_2O$ at 4° and the value −182·85 cal. obtained. The formula for calculating the temperature-coefficient of the fictitious heat of solution given by Cohen and Bruins (*loc. cit.*) is shown to be incorrect, and corrected formulæ have been deduced for the cases applying to hydrates and anhydrous salts. The probable course of the fictitious heat of solution of $CdSO_4,8/3H_2O$, with temperature changes, has been calculated from the values calculated for −7·3°, 4°, and 18°. It is also shown that by making use of a modification of Kirchhoff's formula for the heat of solution, the fictitious heat of solution and the difference between the total energy of elements, may be calculated both for the conditions with and without solid phase if the dependence of the tension of aqueous vapour of the solution on the dilution of the solution and the temperature-coefficient of the solubility of the salt are known. These formulæ hold for both anhydrous salts and hydrates. J. F. S.

Theory of Binary Mixtures. VI. Compressibility of Binary Mixtures. F. DOLEZALEK and F. SPEIDEL (*Zeitsch. physikal. Chem.*, 1920, **94**, 72—110).—The theory of the compressibility of binary mixtures is developed in connexion with the author's theory of binary solutions (this vol., ii, 32). The compressibility of the binary mixtures, benzene–ethylene dichloride, ethyl ether–chloroform, and benzene–carbon tetrachloride has been determined at 24·6° for all possible concentrations up to a pressure

of 600 kilo./sq. cm. The compressibility curve for mixtures of benzene and ethylene dichloride is a straight line at all pressures, which indicates, in keeping with previous vapour-pressure measurements (*loc. cit.*), that both substances are unimolecular and that the compressibility is additive at all concentrations. The compressibility curve for mixtures of ethyl ether and chloroform at lower pressures is strongly convex to the abscissæ axis; consequently there is a strong deviation from simple additivity in the compressibility of these substances. If the amount of complex formation between these substances, previously found from vapour-pressure measurements, is taken into account, the curve becomes a straight line and exact additivity is obtained over the whole range of concentrations. With increasing pressure, in accordance with the theory, the curvature becomes less, and eventually it becomes concave to the abscissæ axis. Mixtures of benzene and carbon tetrachloride exhibit at lower pressures a strongly concave compressibility curve, which is in keeping with the previous vapour-pressure measurements. If the formation of double molecules by the benzene is taken account of, the compressibility for all concentrations becomes additive, and a straight line curve is obtained. With increasing pressure the curve becomes convex, as is demanded by the theory. J. F. S.

Application of the Law of Limiting Densities to Easily Liquefiable Gases and the Atomic Weight of Sulphur. Eugène Wourtzel (*J. Chim. physique*, 1920, **18**, 142—150).—In the light of Guye's recent work (A., 1919, ii, 318), the author has revised certain of his previous calculations (A., 1913, ii, 771), and in particular calculations of the results obtained by Jaquerod and Scheuer on the compressibility of sulphur dioxide. From these calculations he deduces an atomic weight of sulphur, 32·059±0·006. W. G.

The Viscosimeter as a means of Determining Density. J. Holker (*J. Path. Bact.*, 1920, **23**, 185—187).—By combining the formulæ of Ostwald-Poiseuille and of Scarpa (A., 1911, ii, 17), in which the density of the liquid does, and does not, occur respectively, it is possible to find the density by the viscosimeter. The results are in satisfactory agreement, and 2 c.c. or less of liquid are sufficient. J. R. P.

Determination of Density by means of the Pyknometer. Walter Block (*Zeitsch. angew. Chem.*, 1920, **33**, 198—200).—A discussion on the best way of using the pyknometer, attention being directed to sources of error in weighing, influence of atmospheric pressure, etc. W. P. S.

Internal Friction of Binary Mixtures of Liquids. Julius Meyer and Bruno Mylius (*Zeitsch. physikal. Chem.*, 1920, **95**, 349—377).—The density and specific volume of benzene and fluoro-, chloro-, bromo-, and iodo-benzenes have been determined at tempera-

tures from 0° to the boiling point, and from calculations made from the Eötvös rule and the Trouton-Nernst formula it is shown that these substances are probably normal in the liquid condition. The density and specific volume of the binary mixtures of benzene and its halogen derivatives have been determined for various mixtures at temperatures between 0° and 80°. A comparison of the experimental specific volumes with those calculated by the mixture law from the individual specific volumes shows differences which lie within the experimental error, which indicate that the specific volume in these cases is an additive property. The viscosity-coefficient and fluidity of benzene and its monohalogen derivatives have been determined at temperatures between 0° and the boiling point. Below 95° fluorobenzene has a greater fluidity than benzene, despite its larger molecular weight. Above 95° the fluidity follows the expected order, that is, it is inversely proportional to the molecular weight. In all cases the $v\phi$ curves are straight lines, and are in keeping with the Batschinski equation between v and ϕ (A., 1913, ii, 928). The constants a and b of the Batschinski equation have been calculated for all five substances, and the observed and calculated values of ϕ found to be extremely good. The fluidity of the binary mixtures mentioned above has been measured at temperatures 0—80°, and in these cases also the $v\phi$ curves are straight lines. In general, the fluidity and internal friction cannot be calculated from any of the mixture formulæ hitherto applied. The formula $\phi = \phi_1 . b_1/b . p_1(p_1 + p_2) + \phi_2 . b_2/b . p_2/p_1 + p_2$ has been deduced, which applies to all cases. J. F. S.

Examination of Polányi's Theory of Adsorption. LUDWIG BERÉNYI (*Zeitsch. physikal. Chem.*, 1920, **94**, 628—662. Compare A., 1916, ii, 474).—A theoretical paper in which a new method of calculating the partition of the adsorption potential in the adsorption space is developed. The method makes it possible to deduce this function from the isothermals of the adsorbed material above the critical temperature. This method has been applied to the adsorption isothermals of carbon dioxide, nitrogen, ethylene, carbon monoxide, methane, argon, and ammonia by charcoal, and sulphur dioxide and ammonia by silicic acid gels. The data used were obtained from the recent publications of Titoff (A., 1910, ii, 1041), Homfray (A., 1910, ii, 771, 1041), Richardson (A., 1917, ii, 526), and Patrick (Diss., Gottingen, 1914), and the results show that the demands of Polányi's hypothesis are moderately well fulfilled. The theory is applicable to the adsorption of vapours by silicic acid gels. J. F. S.

Adsorption as a Molecular Phenomenon. I. NIKOLAI SCHILOV and LIDIE LEPIN (*Zeitsch. physikal. Chem.*, 1920, **94**, 25—71).—The adsorption of a very large number of electrolytes and other substances from aqueous, alcohol, acetone, and toluene solutions by wood charcoal has been determined. The charcoal used was activated by treatment with superheated steam and purified

by treatment with hydrochloric acid (1:1). The experiments show that adsorption is due to the forces and properties of undissociated molecules. The adsorbent takes part in the process not only by means of its electro-capillary forces, but also by virtue of the whole of its molecular forces. Consequently, adsorption is not to be treated only as capillary chemistry, but also as molecular chemistry. The phenomena of adsorption show themselves to be the more or less complicated result of the molecular forces of the adsorbent, the adsorbed material, and the solvent. The adsorbent exercises a definite field of force, which is dependent on the chemical properties of all the substances concerned in the process, and thereby it becomes to a certain extent specific. For the production of an energetic power of adsorption two conditions are necessary; a difference in structure and definite chemical properties of the adsorbent or its impurities, whereby, however, a chemical reaction need not necessarily be brought about. The molecular field of force of the adsorbent depends on its composition. The adsorption of electrolytes containing either a common anion or cation exhibits characteristic regularities: (1) A series of electrolytes of different cations with the same anion when arranged in groups according to the valency of the cation shows the influence of the atomic weight of the cation and a relationship to its position in the periodic system, in the sense that the adsorption is greater the greater the atomic weight. A further series of the cations may be made with respect to hydrogen, in which those which are more electropositive fall into one group and those which are less electropositive fall into the other. (2) A series of electrolytes of various anions and one cation can be arranged into a number of groups of similar adsorptive properties; it is found that similar types of compounds occur in the same group. The following order of adsorption is found: $H_3XO_3 \rightarrow H_3XO_4 \rightarrow H_2XO_4 \rightarrow HXO_3 \rightarrow HXO_4$. The halogen and organic compounds may also be more or less regularly fitted into the complete series. In each group of a definite type the influence of the relative weight of the anion on the order of the adsorption is clearly marked in the sense that the greater the weight of the anion the more strongly is the substance adsorbed. The adsorption from a mixture of two substances is specific for each pair; it is not directly connected with the degree of dissociation, and cannot be completely explained by the mutual replacement of the substances by one another in the solid phase. The mutual influence of substances on their adsorption shows itself in the liquid phase in consequence of the change in the number of molecules in the solution, due to the formation of solvates or complex molecules. Two cases have been observed: (1) mutual increase in the adsorption of both substances; (2) change in the amount of adsorption of one substance in the presence of a second, which is practically not absorbed at all, for example, the action of neutral salts on the adsorption of acids, alkalis, and other salts with similar ions. The rôle of the solvent in the adsorption process shows itself not only in its own adsorption, but it is of a much

more important and general nature. The solvent, by virtue of its field of force, acts with the adsorbent in the partition of the adsorbed substance between the solid and liquid phases. This view is confirmed from the adsorption from mixed solvents. Here two types of curves and adsorption are observed, which show the dependence of the adsorption on the composition of the binary mixture of solvents: (1) the adsorption shows a definite minimum for a fixed composition of the solvent; (2) all mixtures of two solvents have an adsorption value which is the mean of that of the components.

The adsorption processes have a close connexion with the solubility phenomena, and with some of the facts of chemical kinetics, generally with all those processes in which the concentration of the undissociated molecule exerts itself and in which the influence of neutral salts has been observed. All such phenomena are to be regarded as due to molecular fields of force. J. F. S.

Retention of Gases by Solid Substances. I. and II. Experiments on Carbonyl Chloride. DOMENICO LO MONACO (*Arch. Farm. sper. Sci. aff.*, 1920, **29**, 3—47).—The preparation, properties, and uses of carbonyl chloride are described. The experiments made show that common materials, such as straw, hay, grass, soil, snow, fresh leaves, marine algæ, sawdust, charcoal and cotton, are capable, especially if moist, of absorbing to some extent the asphyxiating gases used in warfare. T. H. P.

Adsorptive Stratification in Gels. IV. SAMUEL CLEMENT BRADFORD (*Biochem. J.*, 1920, **14**, 474—482).—The formation of banded precipitates is due to adsorption of solute from the region between the bands. Only precipitates with great specific surface form bands. This factor is influenced by conditions, such as the reaction medium and the presence of ions. By varying its specific surface, a given substance may be obtained in a banded form or not, as desired; thus, by increasing the dispersity of silver chromate and dichromate, beautiful bands of both substances may be obtained in agar, a medium in which they do not usually form bands. J. C. D.

Surface Tension of Vibrating Liquid Streams Investigated with Water and Aqueous Salt Solutions. H. STOCKER (*Zeitsch. physikal. Chem.*, 1920, **94**, 149—180. Compare Pedersen, A., 1908, ii, 158).—The surface tension of water and of solutions of sodium, potassium, magnesium, calcium, copper, zinc and ferrous sulphates, sodium, potassium, ammonium, calcium, barium and magnesium chlorides, potassium bromide, nitrate, chlorate and perchlorate, sodium chlorate, mercuric cyanide, ammonia, and sucrose has been determined by measuring the amplitude of the wave produced when a stream of the solution emerges from an oval capillary tube under pressure. In the case of water at 18° the surface tension for the vibrating stream is found to be $72{\cdot}43 \pm 0{\cdot}15$ dyne/cm., whilst the accepted value for stationary water is $72{\cdot}94 \pm 0{\cdot}12$ dyne/cm. In the case of

all the solutions examined except that of ammonia, the surface tension under these conditions is found to be somewhat greater than, or in the limiting cases equal to, that of water at the same temperature. J. F. S.

Method of Determining Several Viscosities Simultaneously. J. Holker (*J. Path. Bact.*, 1920, **23**, 177—184).—The method of Scarpa (A., 1911, ii, 17) has been modified, and a method devised for determining several viscosities simultaneously. The method depends on the measurement of two times, t_1 and t_2, the former occupied in drawing up through a vertical capillary sufficient liquid to fill a bulb at the top of this tube, and the latter taken by the liquid in flowing out of the bulb under its own weight. Under constant conditions, the viscosity is then proportional to $t_1t_2/(t_1+t_2)$. J. R. P.

Application of the Theory of Expansion Tension to the Study of Diffusion. L. Gay (*J. Chim. physique*, 1920, **18**, 103—125).—A mathematical discussion of the subject. W. G.

Factors Affecting Rhythmic Precipitation. Alfred E. Koenig (*J. Physical Chem.*, 1920, **24**, 466—477).—A number of experiments are described which show that the uniformity of the bands formed in rhythmic precipitation is uninfluenced by the structure of the gels. This non-uniform structure may be brought about by keeping the gel for some time before the solution is poured on it or by pouring the mixture of sodium silicate and acid just before it sets. The bands of the precipitate may be modified by the presence in the gel of substances such as alcohols, carbamide, and sucrose, all of which modify the rates of diffusion of the reacting substances and the solubility of the precipitated products. The rhythmic bands may be broken up more or less by the presence in the gel of various inert powders unevenly distributed and by the presence of small particles of soap, all of which tend to interfere with the uniform diffusion of the reacting substances. A series of experiments on the formation of rhythmic bands by the interaction in narrow tubes of such gases as ammonia with hydrogen chloride, bromide, or fluoride, and hydrogen sulphide with chlorine or sulphur dioxide has been described, and the relationship with similar reactions in gels pointed out. In addition to the effects of diffusion and the factors that modify it, there are also the effects of the concentrations necessary for precipitation to take place, the velocity of the reaction which forms the precipitate and the degree of supersaturation which the resulting substance may reach in a given medium, before precipitation takes place. J. F. S.

Diffusion and Mobility of Cobalt and Nickel Ions. Elisabeth Rona (*Zeitsch. physikal. Chem.*, 1920, **95**, 62—65).—The diffusion constant, D, for cobalt chloride and nickel nitrate in aqueous and acid solutions has been determined by the method

obtained at 18°: cobalt chloride, in aqueous solution, 0·0127*N*, $D=0·569$; in 0·1*N*-hydrochloric acid solution, 0·1*N*, $D=0·634$; in 0·01*N*-hydrochloric acid solution, 0·01*N*, $D=0·882$; nickel nitrate, in aqueous solution, 0·068*N*, $D=0·802$; in 0·1*N*-nitric acid solution, 0·0413*N*, $D=0·646$; in 0·01*N*-nitric acid solution, 0·0108*N*, $D=0·719$. In aqueous solution and in dilute acid solution the value of *D* decreases with decreasing salt concentration, but increases with decreasing concentration in the more concentrated acid solutions. As the solutions become more dilute the value of *D* approaches a limiting value which is the value of the bivalent ion. From these values, making use of the formulæ $u=Dv/(0·0224v-D)$ and $u=2D/0·0224$, the mobility of the bivalent ions has been calculated and the values Ni=48·0 and Co=47·7 obtained. J. F. S.

Diffusion Experiments with Highly Active Saccharase Preparations. H. von Euler, A. Hedelius, and O. Svanberg (*Zeitsch. physiol. Chem.*, 1920, **110**, 190—216).—Diffusion experiments with different saccharase preparations have given velocities of diffusion of varying magnitudes, and consequently the calculated molecular weights also showed significant variations. The authors conclude that the substrate and the products of the enzymic action do not diminish the size of the colloidal particles of the saccharase, and the velocity of diffusion at the optimum acidity required for the action of the enzyme is not essentially different from that in water. S. S. Z.

Permeability of Thin Fabrics and Films to Hydrogen and Helium. J. C. McLennan and W. W. Shaver (*Phil. Mag.*, 1920, [vi], **40**, 272—280; see Elworthy and Murray, this vol., ii, 508).—The rate of diffusion of hydrogen through a series of balloon fabrics has been determined. The permeability of soap films of thickness corresponding with the reddish-green stage is, for helium, 670 litres per sq. m. per day, and for hydrogen 960 litres per sq. m. per day, at 20°. The rate of transfusion of helium through soap films is 0·70 times that for hydrogen through similar films. The diffusion of hydrogen through water films filling the interstices of wet cotton fabric is very low. J. R. P.

Anomalous Osmosis of some Solutions of Electrolytes with Gold-beater's Skin Membranes. F. E. Bartell and O. E. Madison (*J. Physical Chem.*, 1920, **24**, 444—465).—The osmotic effects of a number of solutions with gold-beater's skin have been examined with the object of ascertaining whether any parallelism exists between the observed effects and the potential difference associated with the same combination. In the case of sucrose it is shown that the rate of osmosis is very nearly proportional to the concentration of the solution. The direction and the magnitude of the flow of solution are, in practically every case, exactly those which would be predicted. If the solution side of the membrane

is of the same electrical sign as the capillary liquid layer the resulting osmosis will be abnormally low or negative, whereas if these parts of the system are of opposite sign the resulting osmosis will be abnormally high. With salts of univalent and bivalent cations the superimposed effect is found to work in opposition to the normal osmosis, with the result that the observed rate of osmosis is less than normal. With salts of aluminium and thorium the superimposed effect works in conjunction with the normal osmosis, and the result is an abnormally large osmosis. Increase in concentration causes but slight increase in the osmosis of solutions of univalent cations, a marked decrease in the osmosis of solutions of bivalent cations and a decidedly greater increase in the osmosis of solutions of tervalent and quadrivalent cations. A logical explanation of the facts seems to be that with dilute solutions of univalent and bivalent cations, the charges of the membrane against the solution is at all times electronegative, which tends to produce an abnormally low osmosis. In the case of solutions of bivalent cations there is a marked tendency to neutralise the negative charge of the membrane, with the result that with more concentrated solutions the membrane approaches the isoelectric point and osmosis now approaches the normal rate. In the case of solutions of tervalent and quadrivalent cations, the sign of the membrane is positive, even with very dilute solutions; this results in an abnormally large positive endosmosis in every case. With two-compartment cells, the concentrations of the solutions on the two sides of the membrane are much more nearly equal than in the one-compartment cell. This is due to the small initial water volume, with the result that the *E.M.F.* of the membrane system is, in this case, much less than in the case of the one-compartment cell. Owing to the smaller potential difference between the two faces of the membrane, the resulting osmosis is in all cases more nearly normal. In the case of solutions of univalent cations, there exists a smaller tendency to negative osmosis, whereas in the case of solutions of multivalent cations, such as thorium and aluminium, there exists a smaller tendency for an abnormally great positive osmosis. In the case of dilute acid the tendency is toward an abnormally great positive osmosis. As the concentration of the acid is increased, the sign of the capillary system is reversed, and the osmotic tendency passes from abnormally great positive to normal, and then to abnormally small, and finally to negative osmosis. In the case of sodium hydroxide a negative tendency persists throughout. At the higher concentrations the electrical factors of the system are such that negative osmosis results Porcelain membranes yield similar results with acids and alkalis.

J. F. S.

Thermodynamics of Mixtures. I. Mario Basto Wagner (*Zeitsch. physikal. Chem.*, 1920, **94**, 592—627).—A mathematical paper in which the equilibrium and reversibility conditions are deduced for purely physical and physico-chemical mixtures.

J. F. S.

may possibly include polyatomic, univalent ions (such as NO_3, CNS, etc.) if these are replaced by monatomic models in which the radius is calculated in such a manner as to give the model the same electrostatic effect which the polyatomic ion possesses. These conclusions are in harmony with the fact that the efficiency of ions increases also with their valency. It is suggested that these rules concerning the influence of the ionic radius can possibly be demonstrated in other phenomena, depending on the electrostatic effect of ions.

H. W.

Relationship between the Non-dissociated Part $(1-a)$ **of Dissolved Salts and the Dielectric Constant** ϵ **of the Solvent.** P. WALDEN (*Zeitsch. physikal. Chem.*, 1920, **94**, 374—404).—From a consideration of a large amount of experimental data it is shown that for a salt in a given solvent the product $(1-a)\sqrt[3]{v}$ is constant over a wide range of dilution, that is, $(1-a)\sqrt[3]{v}=$ const., or $(1-a)=$ const./$\sqrt[3]{v}=$ const. . $c^{\frac{1}{3}}$. The undissociated portion of the electrolyte $(1-a)$ is therefore directly proportional to the linear concentration $c^{\frac{1}{3}}$, or the distance between the molecules in the solution. The constant $(1-a)\sqrt[3]{v}=K$ is practically the same for different typical binary salts in every solvent, provided that the electrolytes are about equally strong in aqueous solution; this constant is characteristic for the binary salts examined, and fluctuates only slightly about a mean value. When the dielectric constant is taken into account, a constant value is obtained which is fundamental to the above-mentioned constant, and this applies to solvents of the most widely differing character; this constant is represented by $(1-a).\epsilon.\sqrt[3]{v}\sim$ const. $\sim 41{\cdot}5$, or $(1-a)\sim$ const. . $c^{\frac{1}{3}}/\epsilon$, that is, in different solvents the undissociated portion of the electrolyte is almost directly proportional to the linear concentration, $c^{\frac{1}{3}}$, and indirectly proportional to the dielectric constant, ϵ, of the solvent.

J. F. S.

Some Thermodynamical Formulæ. RUDOLF WEGSCHEIDER (*Zeitsch. physikal. Chem.*, 1920, **94**, 739—762).—A mathematical paper in which it is shown that the van't Hoff reaction isotherm, which is based on the well-known osmotic pressure equation, for dilute solutions assumes in its deduction that for changing concentration the total pressure changes in such a way that the partial pressure of the solvent remains constant. Consequently, the isothermal does not refer strictly to constant volume relationship. This reaction isotherm, from its kinetic derivation, appears to be applicable for constant volume relations, but strictly it is for this purpose only an approximation formula. The strictly developed reaction isotherm of Planck, which is based on the additivity of the volume and internal energy of dilute solution, is different from that of van't Hoff, and leads to a different law for osmotic pressure, which agrees better with experimental observations than that of van't Hoff, and therefore is to be preferred. There is practically an objection to this formula, for

contains the molecular fraction, and in the case of associated solvents, for example, water, the fraction is not accurately known. The Helmholtz equation, $T(d\Delta A/dT)_v=\Delta U+\Delta A$, is true, not only for constant volume, but also when isothermal processes at various temperatures are carried out in such a way that the change in volume remains the same. If the same isothermal process at different temperatures is carried out in such a way that the change in pressure remains exactly the same, the formula $(d\Delta A/dT)_p = d\Delta pv/dt+(\Delta U+\Delta A)/T$ holds. For complete equilibrium, these formulæ are not applicable. In this case, the equation $d\Delta A/dT = pd\Delta v/dT+(\Delta U+\Delta A)/T$ is applicable. On the basis of the Nernst theorem, a vapour-pressure formula is deduced in which the only approximation made is that the vapour is treated as an ideal gas. On the basis of this formula, equations are developed for the equilibrium constants in gas reactions and for the dependence of the heat of vaporisation on the temperature. J. F. S.

Relationship between the Electrolytic Dissociation and the Dielectric Constant of Solvents. P. Walden (*Zeitsch. physikal. Chem.*, 1920, **94**, 263—294).—Making use of ionisation data previously obtained by the author (A., 1906, ii, 149) and by other investigators, by means of which it was shown that $\epsilon\sqrt[3]{v}=$ constant, it is now shown that all these practically equally strong salts in many solvents at the same dissociation step $\alpha'=\alpha''=$ const., and the corresponding dilution, v, completely fulfil the equation $\epsilon\sqrt[3]{v}=$ const. The degree of dissociation has the value $\alpha'=0{\cdot}50$, $\alpha''=0{\cdot}666$, and in the third case, $\alpha'''=0{\cdot}86$, the dilution varied; for example, with constant degree of dissociation $\alpha'''=0{\cdot}86$, v varied between 16 and 8000 litres. The Ostwald constant,

$$K_0=\alpha^2/(1-\alpha)v,$$

has been calculated for the same degree of dissociation in all solvents; by combining these two equations, the expression $\epsilon/\sqrt[3]{K_0}=$ constant is found for a given α value in all solvents, or the Ostwald constant, $K_0=\epsilon^3$. const., where ϵ is the dielectric constant of the solvent. For infinite dilution, $v=\infty$. $\alpha=1{\cdot}00$ const., and $K_0=(0{\cdot}0054\epsilon)^3$. The dissociation constant for the typical strong binary salts in any solvent can be calculated by means of the equation for the condition when $\alpha=1{\cdot}0$. The values thus obtained agree in many cases exactly, and in others very nearly, with the experimentally determined values. For one and the same salt, tetrapropylammonium iodide, the value of K_0 varies from 0·14 in formamide and hydrogen cyanide to 0·0000017 in benzene and carbon tetrachloride, or approximately in the ratio 00000 : 1. The cause of the decrease in the Ostwald constant with increasing dissociation is probably to be found in the fact that in a given solvent this deviation from the law of mass action is approximately proportional to the concentration of the undissociated salt, that is, for different α-values,

$$K_0':K_0''::(1-\alpha'):(1-\alpha''),$$

or $K_0/(1-\alpha)=$ const. $=K_1$. Transforming this to different solvents, $\epsilon/\sqrt[3]{K_1}\sim$ const. ~ 78. J. F. S.

Molecular Condition of Binary Salts in Weakly Ionising Solvents. Solvation and Polymerism. P. WALDEN (*Zeitsch. physikal. Chem.*, 1920, **94**, 295—373).—The author has examined the condition of binary salts in weakly ionising solvents by means of data previously published by the author himself and others, and also certain other fresh data now published. It is shown that solvolytic dissociation, as well as polymerisation of the dissolved molecules, are common phenomena in non-aqueous solutions. Both phenomena occur simultaneously, particularly in solvents with small dielectric constants, or one and the same solvent can promote a far-reaching solvolysis and a high degree of polymerisation. Acetic acid is a solvent which favours polymerisation. The highest degree of solvolysis is found in media which are practically insulators, such as naphthalene, benzene, carbon disulphide, and chlorinated hydrocarbons, and consequently the solvolytic dissociation cannot depend on ion formation or ion action. The degree of solvolysis of different salts of a common acid is influenced by (*a*) the strength of the base in the salt, and (*b*) the affinity of the medium towards one component of the salt, that is, the power of the solvent to form molecular compounds with the acid or base of the salt. One and the same salt can, according to the solvent, show all possible degrees of polymerisation; the degree of association, x, of its molecules can vary between $x=x$ and $x<1$, and here the dielectric constant of the solvent, E, plays the determinating rôle; the degree of association is greater the smaller the value of E. Quantitatively, it is found for similar degrees of association $x_1=x_2=$constant in various solvents the dielectric constants of which are E_1, E_2, E_3, and the corresponding dilutions v_1, v_2, v_3, that the expression $E_1\sqrt[3]{v_1}=E_2\sqrt[3]{v_2}=$constant, holds. When this expression is re-formed for different degrees of association, the general approximate expression $x\,.\,E\sqrt[3]{v}\sim\text{const}\sim 36$ is obtained. Since these relationships between the degree of depolymerisation of salt molecules and the dielectric constant, E, of the solvent are exactly the same as those between the electrolytic dissociation of the same salt molecules in ionising solvents, it follows that it is likely that depolymerisation occurs according to the scheme $(MeX)_2 \rightleftharpoons \underset{\oplus}{MeX} + \underset{\ominus}{MeX}$. J. F. S.

Structure of Precipitates. SVEN ODÉN (*Svensk. Kem. Tidskr.*, 1920, **5**, 74—85; from *Chem. Zentr.*, 1920, iii, 223).—The author has drawn conclusions as to the structure of precipitates from microscopical investigation and determination of the velocity of sedimentation by the continuous weighing of the sediment falling on a metal plate placed at the bottom of the solution. From sufficiently supersaturated solution, primary particles of the magnitude 1 $\mu\mu$—10 μ are initially formed, which only remain unchanged in exceptional cases. In general, secondary aggregates are further formed, which sink rapidly; these aggregates can frequently be disintegrated by agitation. The author develops

the relationship between the amount of precipitate which has fallen to the bottom and the time by a series of graphs (accumulation graphs), and distinguishes types of reversible and irreversible aggregation. The irreversible aggregates grow continuously, whilst the reversible ones attain a maximal magnitude for which an aggregation period can be found. The influence of the concentration of the electrolyte on the time of aggregation is in harmony with the investigation of Westgren (this vol., ii, 99). The alteration in the time of aggregation with the number of particles was investigated for a constant electrolyte content at the instance of the precipitation of barium sulphate in the presence of citric acid as coagulator, and the results are in agreement with von Smoluchowski's coagulation formula (A., 1917, ii, 297). The cause of the formation of secondary aggregates lies in capillary and adhesion forces, which bring about the coagulation of the colloidal particles. The size of the aggregates increases as the difference in potential between the particles and the liquid diminishes. It has been found possible, under perfectly definite conditions, to calculate the number of primary particles in an aggregate for a suspension of barium sulphate with citric acid as electrolyte. Aggregation and disaggregation have been investigated with increasing additions of this electrolyte. H. W.

Retardation of Crystallisation in Supersaturated Solutions. ERNST COHEN and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1920, **94**, 482—504).—The relationship of the solubility of cadmium iodide to pressure has been examined at 30°, and the relationship between the volume and concentration found to be given by the expression $v_r = 1 \cdot 00435 - 0 \cdot 820924c + 0 \cdot 016857c^2$. The crystallisation of saturated solutions has also been studied, and it is shown that strongly supersaturated solutions may, even in the presence of the solid phase, be caused to crystallise very slowly, in consequence of the presence of small quantities of a third substance. The saturation concentration may apparently, and very slowly, be overstepped at a given concentration in the presence of a small quantity of a third substance. J. F. S.

Symmetry of the Röntgen Patterns obtained by means of Systems Composed of Crystalline Lamellæ, and the Structure of Pseudo-symmetrical Crystals. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 815—830).—Röntgen patterns have been obtained by passing the rays through plates of muscovite (0·32 mm. thick) which crossed one another at various angles (45° or 60°). The patterns obtained indicate that if the central part of a regular complex of crystalline lamellæ, cut perpendicular to a plane of symmetry of the crystals, and crossing at angles $a = 2\pi/n$, be radiated by Röntgen rays, the normal diffraction pattern thus obtained will exhibit an axis of n-fold symmetry, showing, therefore, the image of the original pattern repeated n times. The diffraction image of the dextro-

d lævo-rotatory complexes of this kind are always identical. productions of photographs of the patterns obtained are given the paper. J. F. S.

Bragg's Work and the Law of Definite Proportions. . QUARTAROLI (*Gazzetta*, 1920, **50**, ii, 60—64).—From the ivestigations of Bragg on crystals of sodium chloride and nalogous compounds, diamond, pyrites, etc., it follows that such rystals represent a homogeneous mixture of atoms distributed egularly in space. For instance, in the case of iron pyrites, the elementary cube has four atoms of iron at alternate corners and an atom of sulphur in the interior. An aggregation of n^3 such cubes has the composition $Fe_{(n+1)^3}S_{2n^3}$, which approximates to FeS_2 when n is very large, but when n is 50 and the aggregate of the order of magnitude of granules visible by the ultramicroscope, the composition is represented by the formula $FeS_{1\cdot885}$. It is therefore possible that continuous variations may occur in the chemical composition of micro-crystals in accordance with the magnitude of such crystals when deposited; with pyrites, the composition might vary from Fe_4S to FeS_2. T. H. P.

The Reversal of the Sign of the Charge of Collodion Membranes by Tervalent Cations. JACQUES LOEB (*J. gen. Physiol.*, 1920, **2**, 659—671).—Tervalent cations cause a collodion membrane covered with a protein film to be charged positively, whilst they do not produce such an effect on collodion membranes not possessing a protein film. The same has been found for the reversal of the sign of charge of the membrane by acid. This reversal in the sign of charge of the membrane by tervalent cations occurs on the alkaline side of the isoelectric point of the protein used, whilst the reversal by acid occurs on the acid side of the isoelectric point. The reversal seems to be due to, or to be accompanied in both cases by, a chemical change in the protein. The chemical change which occurs when the hydrogen ions reverse the sign of charge of the protein film consists in the formation of a protein-acid salt, whereby the hydrogen ion becomes part of a complex protein cation, whilst the change which takes place when tervalent cations reverse the sign of charge of the protein film consists in the formation of an insoluble, and therefore sparingly or non-ionisable, metal proteinate. H. W.

A Series of Abnormal Liesegang Stratifications. EMIL HATSCHEK (*Biochem. J.*, 1920, **14**, 418—421).—A number of such abnormalities, which were encountered when attempts to obtain stratification of calcium phosphate in gelatin were made, are described and illustrated. It is obviously impossible to attemp an explanation of these abnormal results in the present unsatisfactory state of knowledge regarding the normal phenomenon. J. C. D.

Application of Smoluchowski's Equation to the Chang with Time of the Number of Particles in an Emulsio P. C. VON ARKEL (*Physikal. Zeitsch.*, 1920, **21**, 465—467).—Acco

ing to Smoluchowski (see A., 1916, ii, 302), the formula deduced by him for the Brownian movement is in agreement with the observations of Svedberg ("Existenz der Moleküle," 1912, p. 148). It is shown that this agreement is not sufficiently close when all the deductions of Smoluchowski are compared with the experimental numbers. The differences are probably to be explained by the incompleteness of the series of observations rather than by defects in the theory. J. R. P.

Conductivity Depression and Adsorption by Lyophile Colloids. M. Polányi (*Biochem. Zeitsch.*, 1920, **104**, 237—253).—The name "*L*-effect" is given to the percentage by which the electrical conductivity of a mixture of electrolyte and colloidal solution falls short of that of the colloid-free disperse medium of the same mixture; the specific *L*-effect refers to 1 gram of dissolved colloid. Whereas crystalloids lower the conductivity in the same measure as they raise the viscosity of the solvent, colloids depress the conductivity far less than the fluidity; this discrepancy indicates that the ions in colloidal solutions set in motion only the disperse medium, and not, to any extent, the colloidal particles.

The method employed to measure the *L*-effect consists in leaving a parchment thimble containing a colloidal solution immersed in a definite quantity of water until the diffusion reaches a condition of equilibrium, and then measuring the electrical conductivities of the colloidal solution remaining inside the thimble and of the pure, disperse medium from the outer vessel. The results thus obtained with various colloids and electrolytes are given, and calculations made of the "non-conducting space," that is, the volume per gram of colloid calculated on the assumption that the colloidal particles, by their mere presence, diminish the number of ions per c.c. and prolong their paths. This assumption almost suffices to account for the magnitudes found for the *L*-volume.

The swelling of colloidal substances indicates that part of the disperse medium is held by the colloidal particles, and the assumption may be made that the small amounts by which the non-conducting space exceeds the specific volume of colloidal substances, namely, 0·8, have their origin in the increase in size of the colloidal particles caused by the aqueous envelope. Explanations of the depression of the conductivity of electrolytes by colloids other than the purely mechanical one appear to be excluded by the following observations: (1) The *L*-effect of casein is the same when the casein is dissolved as sodium caseinate as when it is simply suspended in the coarsely granular, undissolved condition. (2) The *L*-effect is, within wide limits, proportional to the concentration of the colloid. This hypothesis assumes that all the ions in an electrolyte are influenced to the same extent by a colloid, but since Cybulski and Dunin-Borkowski (*Krak. Anz.*, 1909, 660) have found that the transport numbers are altered considerably by the presence of colloids, the author makes the further assumption that the aqueous envelopes of the colloidal particles are permeable to varying degrees

for different ions; this assumption also serves to explain the effect of the colloid on the diffusion potential.

The adsorption of electrolytes in colloidal solution is also considered, use being made of the equilibrium dialysis to determine the "non-dissolving space," that is, the space taken up by the colloid. If the specific volume of the colloid is 0·8, positive or negative adsorption is shown by the non-dissolving space per gram of colloidal substance being smaller or larger than 0·8. It has been shown thermodynamically that substances which increase (or diminish) the osmotic pressure of colloids are adsorbed positively (or negatively) (A., 1914, ii, 720). Since continued diminution of the osmotic pressure must lead finally to coagulation, the obvious conclusion is that coagulating substances must be negatively, and those which hinder coagulation positively, adsorbed. This conclusion requires experimental proof, but is supported by the fact that dextrose, which retards the coagulation of albumin considerably, is positively adsorbed by albumin to a marked extent.

T. H. P.

Undamped Oscillations derived from the Law of Mass Action. ALFRED J. LOTKA (*J. Amer. Chem. Soc.*, 1920, **42**, 1595—1599).—A theoretical paper in which it is shown that in certain circumstances conditions may be obtained in an homogeneous system for the production of undamped oscillations in the absence of any geometrical cause. J. F. S.

Statistical Meaning of the Thermodynamical Functions. KARL F. HERZFELD (*Zeitsch. physikal. Chem.*, 1920, **95**, 139—153). —A mathematical paper in which a number of statistical formulæ are discussed and the difference between the external work and the added heat pointed out. The dependence of the total energy on the temperature is discussed. Using the same formulæ, the conditions of chemical equilibria and chemical potential for gaseous and dilute solution systems are developed. The equations deduced in the last cases are then applied to the formulæ of von Laues.

J. F. S.

Temperature-coefficients of the Action of Saccharase. HANS VON EULER and INGVAR LAURIN (*Zeitsch. physiol. Chem.*, 1920, **110**, 55—92).—Determination of the velocities of inversion by saccharase at pairs of different temperatures shows that the constant A of Arrhenius's temperature formula (this vol., i, 506) varies with the temperature in accordance with the equation $A = 11{,}400(1 - 0{\cdot}009t)$, which is in agreement with the results of Kjeldahl (A., 1883, 225) and O'Sullivan and Tompson (T., 1890, **57**, 834).

There is no theoretical basis indicating the independence of the constant A on the temperature; according to Arrhenius (A., 1889, 1103), A represents the heat change of the reaction, and there is no reason to assume that this heat change must always be independent of the temperature. On the other hand, the

Arrhenius temperature formula agrees well with the experimental results over a wide range of temperature, especially for the inversion of sucrose by acids. On the assumption that the velocity of the enzymic inversion of sucrose is proportional to the concentration of the complex molecule, sucrose–enzyme, the temperature-coefficient of the inversion is determined by the following magnitudes: (1) the influence of the temperature on the concentration of the active enzyme; (2) the influence of the temperature on the reactivity of the compound, sucrose–enzyme (and the reactivity of the water); and (3) the alteration of the equilibrium, sucrose: enzyme, with temperature. The last of these may be determined quantitatively on the basis of Michaelis and Menten's theory (A., 1913, i, 540), according to which $[S][E-\phi]=K[\phi]$, where $[S]$ is the concentration of the free substrate, $[E]$ the total molar concentration of the enzyme, $[\phi]$ the concentration of the combined enzyme or of the compound, sucrose–enzyme, and K_M the equilibrium constant. The value of the velocity of inversion is given by $v=C[\phi]=C[E][S]/([S]+K_M)$, C being a proportionality factor; influence (2) is expressed in the factor C and influence (3) in K_M.

The authors have measured the values of the constant K_M of the equilibrium between sucrose and enzyme for the temperature interval 0—40°, use being made of methods essentially the same as that of Michaelis and Menten (*loc. cit.*). At 25° and for the optimal acidity ($p_H=4{\cdot}5$), the value of K_M is found to be 26.10^{-3}, which remains unchanged over the acidity region $p_H=3{\cdot}35$—$5{\cdot}65$; the above authors gave 16.10^{-3}. Three-fold increase of the concentration of the enzyme is without influence on the value of K_M.

The equilibrium constants of the equilibrium $[S][E-\phi]=K_M\phi$, obtained for the temperatures 1°, 15°, 25°, and 39°, show that the equilibrium is altered approximately by 1% per degree rise of temperature; the values obtained at these temperatures agree well with those calculated with the help of the heat of dissociation, Q, this being found by the equation $Q=-RT^2.d\log k/dT=-[4{\cdot}58(\log K_2-\log K_1)T_1T_2]/(T_2-T_1)$ to have the mean value 2000 cals.

As regards the great difference between the temperature-coefficients for enzymic inversion (9400 at 20°) and acid inversion (25,600 at 20°), the results obtained show that this is not due to abnormal alteration of the equilibrium enzyme: sucrose, but that it can depend only on increase in concentration of the compound, sucrose–acid, as the temperature rises. T. H. P.

Ester Formation in Absolute Ethyl Alcohol. HEINRICH GOLDSCHMIDT, J. ANDERSON, M. FEIGL, G. GÖRDITZ, J. SCHJERVE, L. SVENDSEN, A. THUESEN, O. UDBY, and P. WRAA (*Zeitsch. physikal. Chem.*, 1920, **94**, 233—253).—The rate of esterification of acetic acid in absolute alcohol has been determined with trichlorobutyric, trichloroacetic, picric, hydrochloric, and sulphosalicylic acids as catalysts. Similar experiments with the same

catalysts have been carried out for the rate of esterification of propionic, *n*-butyric, *iso*butyric, *n*-valeric, *iso*valeric, pivalic, heptoic, phenylacetic, phenylpropionic, and glycollic acids. The results in all cases show that the rate of esterification is satisfactorily represented by the formula $k = c[K_A\gamma + K_B(1-\gamma)]$. The results also show that both the ions and the undissociated acid act catalytically. The velocity-constant for the undissociated portion of the catalyst, K_B, is in general the greater the greater the affinity-constant of the catalyst. The relationship of K_A, the velocity-constant of the reaction catalysed by the hydrogen ions, to K_B is in general, for the different acids with one and the same catalyst, not constant. The relationship K_A/K_B in the case of hydrochloric acid as catalyst is not equal to unity, but considerably greater, in all cases investigated. For calculating the present results, the degree of dissociation of picric acid was necessary. This has been obtained from electro-conductivity determinations of aniline picrate in alcohol solution. The value $\lambda_\infty = 49$ is obtained. The value of K_A and K_B are given for all cases examined. J. F. S.

Formation and Hydrolysis of Lactones. A. KAILA (*Zeitsch. physikal. Chem.*, 1920, **94**, 111—128).—A theoretica paper in which the experimental results of P. Henry (A., 189 ii, 1303) on the rate of formation of the lactones of γ-hydroxy butyric acid and γ-hydroxyvaleric acid have been recalculate It is shown that, in the above-named reactions in aqueous solutio abs strong acids as catalysts, the catalytic action of the undi

Staed acid, if it is present at all, is in any case much small
KARL hat of the hydrogen ion. The velocity-coefficients have be
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are disc 223) on the hydrolysis of γ-butyrolactone and γ-valer
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be ascertained from the velocity-constant of a reaction carried out with the mixture and a given reagent, such as the rate of hydrolysis of a mixture of esters with alkali hydroxide. Two methods are elaborated, the first, a graphic method which is applicable when the reaction-constants of the pure components, as well as that of the mixture, are all known, and the second, a mathematical method applicable when the reaction-constants for the mixture and one component are known, and when one of the components reacts much more rapidly than the other. The methods are applied to the reaction of barium hydroxide on mixtures of α- and β-glyceryl chlorohydrin and to the hydrolysis of a mixture of ethyl butyrate and acetate by the same reagent. The results show the value and trustworthy character of both methods. J. F. S.

Ageing of Colloidal Catalysts (Platinum, Palladium). GREGORIO DE ROCASOLANO (*Compt. rend.*, 1920, **171**, 301—303).—The catalytic activity of electrosols of platinum and hydrosols of palladium increases at first with age until it reaches a maximum, and then decreases. W. G.

Influence of the Substrate Concentration on the Rate of Hydrolysis of Proteins by Pepsin. JOHN H. NORTHROP (*J. gen. Physiol.*, 1920, **2**, 595—611).—It is pointed out that the apparent exceptions to the law of mass action found in enzyme reactions are also encountered in catalytic actions in strictly homogeneous solutions. These deviations may be explained by the hypothesis that the active mass of the reacting substances is not directly proportional to the total concentration of substance taken. In support of this suggestion, it is shown that for any given concentration of pepsin the relative rate of digestion of concentrated and of dilute protein solutions is always the same. If the rate of digestion depended on the saturation of the surface of the enzyme by substrate, the relative rate of digestion of concentrated protein solutions should increase more rapidly with the concentration of enzyme than that of dilute solutions. This is found not to be true, even when the enzyme could not be considered saturated in the dilute protein solutions.

The rate of digestion and the conductivity of egg-albumin solutions of different concentration are found to be approximately proportional at the same P_H. This agrees with the hypothesis first expressed by Pauli, that the ionised protein is largely or entirely the form which is attacked by the enzyme. The rate of digestion is diminished by a very large increase in the viscosity of the protein solution; this effect is probably mechanical in nature and due to the retardation of the diffusion of the enzyme. H. W.

Catalysis with Platinum Black. II. E. OLIVERI-MANDALÀ (*Gazzetta*, 1920, **50**, ii, 81—89. Compare A., 1916, ii, 615).—According to Traube's hypothesis, the function of platinum black in the catalysis of hydrogen peroxide is represented by the equa-

ions: $nPt + yH_2O_2 = Pt_nO_y + yH_2O$ and $Pt_nO_y + yH_2O_2 = nPt + yH_2O + yO_2$. This hypothesis scarcely seems capable of extension to the catalyses of ammonium nitrite, azoimide, hydroxylamine, and hydrazine, represented by the respective equations $NH_4NO_2 = 2H_2O + N_2$, $3N_3H = 4N_2 + NH_3$, $4NH_3O = 2NH_3 + N_2O + 3H_2O$, and $2N_2H_4 = 2NH_3 + N_2 + H_2$, especially when the absence of oxygen from azoimide and hydrazine is considered. It may be that the catalyst reacts with water, forming a platinum oxide and hydrogen, catalytic oxidations and reductions being thus rendered possible. In this way, it is possible to explain the different steps in the three different catalytic decompositions of hydrazine, namely, (1) $2N_2H_4 = 2NH_3 + H_2 + N_2$, (2) $3N_2H_4 = N_2 + 4NH_3$, and (3) $3N_2H_4 = 2N_2 + 2NH_3 + 3H_2$.

A similar explanation may be given for the catalysis of hydroxylamine by platinum black (Tanatar, A., 1902, ii, 386, 495). The equation given above indicates a reaction of the fourth order for this decomposition, but the author's study of the velocity shows that the reaction is of the first order, and that it is the result of a number of simple reactions.

The mechanisms of the catalyses of azoimide (Cooke, P., 1903, 213) and ammonium nitrite (Vondráček, A., 1904, ii, 390) are also discussed. T. H. P.

Catalytic Actions at Solid Surfaces. V. Rate of Change Conditioned by a Nickel Catalyst and its Bearing on the Law of Mass Action. E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1920, [*A*], **98**, 27—40. Compare this vol., ii, 422, 423).—The curves representing the hydrogenation of methyl cinnamate, anethole, and safrole at 140° and 180° in the presence of nickel have a form for 60—80% of their length represented by $K = v/t$, which indicates complete hydrogenation. In the case of *iso*eugenol and coumarin, the hydrogenation curves show a transition from a linear to a logarithmic curve. In the case of ethyl cinnamate, instead of passing a continuous stream of hydrogen over the catalyst, the tube was closed at one end; under these conditions, the results show: (i) with increasing purity of hydrogen, the ratio, v/t, approaches the constancy characteristic of hydrogenation in a continuous stream of hydrogen; (ii) the values of $K' = 1/t \log V'/(V' - v)$ increase throughout, but become more nearly concordant as the purity of the hydrogen decreases. As the purity of the hydrogen and the speed of the action, measured by v/t, increase, the absolute value of the constant,

$$K'' = 1/t \log V''/V'' - v,$$

falls, that is, the rate at which the gas space becomes filled with impurity is smaller the purer the hydrogen. The hydrogenation curve of linseed oil shows an initial linear portion of about 30% of the whole curve, which corresponds with the hydrogenation of all the linolenin and most of the linolein; a very abrupt curvature then sets in, and this is followed by an approximately linear curve at a much lower slope. These experiments were carried out with 200, 300, and 400 grams of oil, and of 0·45 and 1·5 grams of

nickel. They show: (i) that the factor v/t depends on the mass of nickel present, (ii) the impurities in the oil gradually affect the catalyst, and (iii) with the smaller quantity of nickel the rates are practically the same for quantities of 200 and 300 grams of oil, but with 400 grams the linear portion of the curve is shortened, owing to the increased effect of the impurity.

It is shown that the hypothesis of unstable intermediate compounds between catalyst and reacting substances offers a reasonable explanation of the mechanism of "so-called" heterogeneous catalytic actions, and in particular for reactions of the types: (i) Action of enzymes on sugar derivatives in aqueous solution. (ii) The Sabatier catalyses of organic compounds in the presence of finely divided metals or metallic oxides, including hydrogenation and dehydrogenation, hydration and dehydration, formation of ethers and ketones, the specific action of finely divided metals on the vapours of aliphatic acids, and the combined dehydration and condensation processes effected by certain metallic oxides, leading to the production of ethers, amines, mercaptans, and esters from alcohols and phenols. (iii) The interaction of carbon monoxide and steam conditioned by various solid substances. J. F. S.

Catalytic Activity of Copper. I. W. G. PALMER (*Proc. Roy. Soc.*, 1920, [*A*], **98**, 13—26).—The mechanism of the catalytic oxidation of ethyl alcohol and *iso*propyl alcohol by metallic copper has been studied at temperatures up to 320°. It is shown that in no circumstances, even when the copper is alloyed with zinc, does electrolytic copper exert any influence on either of these alcohols. The oxidation is effected by copper produced by the reduction of copper oxide. The reaction has been carried out in such a way that the rate is automatically registered by the liberated hydrogen. In the present case, the initial period of the reaction alone has been considered. The experimental facts are best interpreted by assuming that alcohol is selectively adsorbed by copper from a mixture of alcohol and aldehyde vapours, so that during dehydrogenation the surface of the copper is covered by a layer of alcohol molecules, and adsorption and consequent destruction of the aldehyde prevented. If it be supposed that dehydrogenation of alcohol involves three stages, (i) adsorption of alcohol molecules over the surface of the copper, (ii) activation of certain alcohol molecules by absorption of energy, and (iii) evaporation of acetaldehyde and hydrogen from the adsorption surface into the alcohol stream flowing past the catalyst, then the process bears a close physical analogy to the escape of ions from a heated solid.

J. F. S.

Conditions of Stability of Atoms. FÉLIX JOACHIM DE WISNIEWSKI (*Arch. Sci. phys. nat.*, 1920, [v], **2**, 301—308).—A mathematical paper in which the stability of atoms of the Bohr type is derived from the assumption that the electrical potential energy of the atom is a positive function. J. R. P.

Constitution and Configuration of the Atom. EMIL KOHLWEILER (*Zeitsch. physikal. Chem.*, 1920, **94**, 513—541).—A theoretical paper in which the views recently advanced by the author on the constitution and configuration of the atoms (A., 1918, ii, 286, 304; 1919, ii, 21) are extended and modified with the object of making the hypothesis include all the elements, particularly those of the rare earths. On the basis of the present hypothesis, a spatial representation of the periodic system is developed which arranges the elements according to a cascade system, in which the steps from one plane to the next are occupied respectively by cobalt and nickel, rhodium and palladium, the metals of the rare earths, and iridium and platinum. J. F. S.

Structure of the Atomic Nucleus. E. GEHRCKE (*Sitzungsber. Heidelberger Akad. Wiss., Math.-naturwiss. Kl.*, [*A*], 1919, pp. 19; from *Chem. Zentr.*, 1920, iii, 169—170).—In continuation of the models developed previously for the lithium, glucinum, boron, and carbon atoms (this vol., ii, 241), the author now puts forward structures for the atomic nuclei of the other elements to the end of the periodic scheme. The fundamental hypothesis is that the atomic nuclei of the higher elements are merely repetitions of those of a lower horizontal series of the periodic system, with the difference that the nucleus is surrounded by a ring of α-particles. Thus, for example, the atomic nucleus of sodium is identical with a lithium nucleus surrounded by a ring composed of four α-particles, whilst, similarly, the potassium nucleus is identical with a sodium nucleus surrounded by a ring of four α-particles. Isotopes are possible for several atoms which differ from one another by an α-particle in the ring enclosing the central nucleus. The number of α-particle rings is considerable in the case of the higher elements. Every element would thus appear as a compound of a primal element, $H^{\cdot}$, and electron, arranged according to a systematic and not too complicated plan. Order is thus introduced into the relationship between atomic weight and atomic number, and explanations are found for a lengthy series of empirical observations, such as the chemical similarity of the rare earths, the spaces in the periodic system, etc. H. W.

Atomic Weights and Atomic Numbers. STEPHEN MIALL (*Chim. et Ind.*, 1920, **4**, 189—192).—If graphs are plotted of which the ordinates represent atomic weights and the abscissæ the atomic numbers, that is, the positions of the elements in the periodic system, the series form nearly parallel curves. For the group of elements helium to nickel, and copper to tungsten, the curves are represented by the equation $y = 2x + a$, and for the group platinum to uranium by $y = 3x + a$. The lack of relationship between atomic weights and the properties of elements is assumed to be due to the factor a, which is known as the "inert weight"; the "active weight" of the atom determines the valency of the element, and not necessarily its chemical activity. Hydrogen does not conform

to the equation $y=2x+a$; it may be represented by $y=x$ or $y=\frac{1}{2}x+\frac{1}{2}$, but probably its atom contains no inert weight.

The graphs indicate that 2·5 units of the atomic weight are normally active, whilst one unit may be chemically inactive. Assuming the atoms to consist of particles equal to 0·5 of unity, it is probable that one particle is active, and that two particles may be either active or inactive. The equation $y=Mx+a$ represents the atomic weights of all the elements, x being the atomic number and a a small whole number, the properties of the elements being independent of a. W. J. W.

Periodic System of the Elements in the Light of the Theory of Radioactive Degradation. F. KIRCHHOFF (*Zeitsch. physikal. Chem.*, 1920, **94**, 257—262).—A theoretical paper in which the position in the periodic system and the possible genesis of the elements are considered in the light of the known facts of radioactive degradation. It is shown that the atomic weights, A, of the more stable elements, which are functions of the atomic number, M, and I, the number of nucleus electrons, in that $A=2(M+I)$, are periodic functions of I, since in certain parts of the periodic system A remains practically constant, and then commences to change regularly, and this reappears periodically. J. F. S.

Deduction of the Smoluchowski Formula of Spatial Partition of Particles in a Kinetic Field. R. LORENZ and W. EITEL (*Zeitsch. physikal. Chem.*, 1920, **94**, 254—255. Compare A., 1914, ii, 451).—A correction of an intermediate stage in the deduction of the Smoluchowski formula previously published (*loc. cit.*). J. F. S.

Metastability of the Elements and Compounds as a Consequence of Enantiotropy or Monotropy. I. ERNST COHEN and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1920, **94**, 450—464. Compare A., 1916, ii, 183).—A theoretical paper in which reasons for the failure of other workers in reproducing the authors' previous work on metastable varieties of metals are enumerated. It is also pointed out that metastable varieties of elements and compounds are of much more frequent occurrence than has been generally believed. A general discussion of the conditions under which such metastable varieties may be obtained is entered into, and particular stress is laid on the influence of minute traces of impurities. J. F. S.

A Method for the Experimental Proof of the Molecular Theory and the Avogadro-Loschmidt Number. A. VON SZENT-GYÖRGYI (*Zeitsch. physikal. Chem.*, 1920, **95**, 247—250).—A method is indicated by which the Avogadro number may be experimentally determined. The method consists in adding to an albumin suspension of known content various solutions of known concentration of aluminium chloride, and examining the charge

on the particles. When exactly the correct quantity of aluminium chloride has been added, so that the particles all change the cataphoresis from positive to negative, it is possible to calculate the Avogadro number on the assumption, which is substantiated, that one ion discharges one albumin particle. J. F. S.

Nature of the Chemical Bond; an Attempt to Find a Common Cause for the Conceptions; Auxiliary Valency and Molecular Bond. F. Hocheder (*Zeitsch. physikal. Chem.*, 1920, **94**, 129—148).—A theoretical paper in which an hypothesis is put forward to explain the origin of subsidiary valencies, and, at the same time, to account for the formation of double compounds, complexes, and hydrates. It is assumed, in keeping with Bohr's hypothesis, that the ordinary chemical bond is due to an oscillating electron between the two atoms concerned; this is regarded as an electric current flowing in a close circuit in which the atoms concerned lie. When two such circuits lie parallel to one another, there will naturally be an attraction set up between them, and this could well be powerful enough to hold the two compounds together, that is, a molecular compound would be formed. For such a compound to be stable, it is necessary that the bonds in the individual compounds should be parallel, and that the current in each flowing at the same rate and in the same direction, that is, the periodicity of the electron oscillation is the same in both cases. The hypothesis is illustrated in connexion with a number of well-known double compounds, and it is discussed in connexion with Werner's co-ordination theory. As will be seen a new type of spatial structure is involved in this hypothesis.

J. F. S.

Negative Valencies. D. Strömholm (*Zeitsch. anorg. Chem.* 1920, **111**, 237—242).—A theoretical paper in which the valencie of negative elements are considered. It is pointed out that whe a negative element forms compounds in which it acts with differen valencies, these always differ by two, that is, the valencies o negative elements are always saturated in pairs. This is to b explained by assuming that in the negative elements the valenc electrons are grouped together in pairs. The valency figure of which dominates the negative valencies is therefore to be regarde as made up of four pairs of electrons, which constitute a con pletely saturated system. This is governed by the tetrahedr symmetry, and the stereochemical data show that, in the case (those elements which can enter into combination by their negativ valencies, the symmetry relationships are determined by tł tetrahedron. J. F. S.

Chemical Concepts of the Ancient Orientals. Y. I Chen (*Science [China]*, 1920, **4**, 262—284).—Chemical knowled in ancient China seems to have attained a rank comparable that reached in Egypt. The four elements, earth, fire, air, wate formed the basis of a later chemical philosophy, which w

developed quite independently of the Occident. Theories were developed similar to those of Aristotle and of the earlier iatro-chemists. The Orient also produced a system of iatro-chemistry founded on the "Ben Tsao" written in 2838 B.C. This medical chemistry ceased its development from about 1200 A.D.

CHEMICAL ABSTRACTS.

An American Edition of the Elementary Treatise of Chemistry by Lavoisier, published at Philadelphia in 1799. GRAHAM LUSK and JEAN LE GOFF (*Bull. Soc. chim.*, 1920, [iv], **27**, 667—673).—A brief description of the various French editions of Lavoisier's work, and the subsequent English, Spanish, Italian, and Dutch translations, together with an account of an edition published in Philadelphia in 1799. W. G.

Improved Form of U-Tube. E. R. DOVEY (*Analyst*, 1920, **45**, 333).—The two limbs of the U-tube are brought together so that the rims at the top are in contact; the bend at the bottom of the tube is constricted, and a perforated Gooch disk is placed at the bottom of each limb. W. P. S.

Extraction Apparatus with Vapour Stirring. P. WAENTIG (*Text. Forsch.*, 1920, **2**, 61—62; *Chem. App.*, 1920, **7**, 92—93; from *Chem. Zentr.*, 1920, iv, 265).—In order to allow the vapours of the boiling liquid to enter the extraction space, and thus to utilise their latent heat in the Soxhlet apparatus, the lower tube of the latter is sunk so deeply into the liquid in the boiling flask that its open end becomes clear of the surface of the liquid only when the extraction tube is filled almost to the level of the top of the syphon tube. To allow the vapour from the boiling liquid to pass into the syphon tube, the latter is somewhat lengthened, and terminates just above the level of the boiling liquid in the flask. H. W.

Air-oven Thermo-regulator. H. M. ATKINSON (*J. Soc. Chem. Ind.*, 1920, **39**, 298T).—A cylindrical float, loaded slightly with mercury and having its upper end in the form of a capillary, is contained in one limb of a U-tube filled partly with mercury. The capillary extends upwards into a tube passing through the cork closing this limb of the U-tube, the shoulder of the float and the end of the tube being ground to form a gas-tight joint when the float rises. The gas enters through a side-tube above the mercury-level, passes between the neck of the float and the tube, then into the latter and thence to the burner. The other limb of the U-tube connects with a bulb in the oven. When the float rises and cuts off the gas supply, a small quantity of gas is allowed to pass through a hole in the side of the float and escapes through the capillary to the burner, the capillary thus acting as a by-pass. W. P. S.

Inorganic Chemistry.

Preparation of Ammonia-free Water. GERALD C. BAKER (*J. Ind. Eng. Chem.*, 1920, **12**, 798—799).—Water free from ammonia may be obtained by passing distilled water through a moderately deep layer of permutite (a complex hydrated sodium aluminium silicate); a layer 30 cm. deep and 20 cm. in diameter will remove the ammonia from 450 litres of water. The activity of the permutite may be regenerated by treatment with 10% sodium chloride solution. The disadvantage of the method is that it gives a water of higher mineral content. W. P. S.

Rate of Decomposition of Hydrogen Peroxide in the Presence of Iron Ions. JOSEPH VON BERTALAN (*Zeitsch. physikal. Chem.*, 1920, **95**, 328—348).—The rate of decomposition of hydrogen peroxide at 40° has been determined in the presence of ferrous sulphate or ferric sulphate and a little free sulphuric acid ($0 \cdot 01M$). The reaction occurs in all cases as a typical unimolecular catalytic process. The velocity of reaction in acid solutions and in the presence of either ferrous or ferric ions is directly proportional to the concentration of the hydrogen peroxide and that of the iron ions, and inversely proportional to the hydrogen-ion concentration or the concentration of the free acid. The velocity of the reaction is entirely independent of the state of oxidation of the iron ions, and the catalytic action depends on the total amount of iron present, no matter what its state of oxidation. The temperature-coefficient of the reaction is 3·25 for 10°. J. F. S.

Solubility of Halogens in the Corresponding Hydracids and Alkali Salts. II. E. OLIVERI-MANDALÀ (*Gazzetta*, 1920, **50** ii, 89—98. See this vol., ii, 542).—The solubilities of chlorine in sodium chloride solutions and hydrochloric acid, and that of bromine in hydrochloric and hydrobromic acids, have been measured.

The results confirm the observation that the solubility of chlorine is greater in hydrochloric acid than in water, whereas the presence of sodium chloride diminishes the solubility in water by amounts increasing with the proportion of salt present. The coefficient of solubility of the chlorine diminishes as the concentration of sodium chloride increases, but the expression $(\alpha' - \alpha)/M^{\frac{1}{3}}$ gives constant values, α' and α representing the coefficient of absorption of chlorine in water and sodium chloride solution respectively, and M the concentration of the salt in gram-mols. per litre of solvent. This empirical formula has been verified (Gordon, A., 1896, ii, 154) for the solubility of indifferent gases in aqueous solutions of electrolytes, so that chlorine behaves differently from the other halogens, which exhibit almost the same solubility in solutions of the corresponding hydracids and in those of the alkali salts. T. H. P.

Action of Light on Moist Chlorine. ERNST RADEL (*Zeitsch. hysikal. Chem.*, 1920, **95**, 378—383).—Using the ultra-microscopic iethod, the reaction between chlorine and hydrogen has been udied. It is found that when moist chlorine is illuminated an iduction period is set up which varies between 1/100 sec. and 0 secs., after which a fine fog is produced which rapidly forms rops. On removing the light the particles become smaller, and ventually disappear. The same effect is observed when the chlorine ionised by a spark from an induction coil or by the light from a esla transformer. Radiation from polonium or radium bromide as the same effect, but much weaker. J. F. S.

Concentration of the Lighter Isotope of Iodine. EMIL OHLWEILER (*Zeitsch. physikal. Chem.*, 1920, **95**. 95—125).—In an irlier paper (this vol., ii, 610) the author has shown that in all robability five isotopes of iodine exist which have atomic weights 22, 124, 126, 128, 130, depending on their origin. This involves fferences varying between −3·88% and +2·43% from the mean ilue, 126·92, of the atomic weight. Vapour density determinations ive been carried out by the Dumas method with iodine which has en twice sublimed, thrice sublimed, recrystallised from carbon sulphide, separated by diffusion, and fractionated. Ten experients with twice sublimed iodine give an atomic weight which has mean divergence of 2·04% from the accepted value; eight experients with fractionated iodine give a mean divergence of 1·33%. f twenty-seven experiments, not one gives atomic weights which e equal to or less than the accepted value. The lowest value tained for the atomic weight is 128·22. An apparatus is described means of which a possible separation of the isotopes may be ought about by diffusion. J. F. S.

Preparation of Iodic Acid and its Anhydride. ARTHUR LAMB, WILLIAM C. BRAY, and WALTER J. GELDARD (*J. Amer. iem. Soc.*, 1920, **42**, 1636—1648).—A simple and rapid method s been developed for the preparation of iodine pentoxide, which pends on the oxidation of iodine to iodic acid by means of —26% chloric acid solution, the evaporation of the solution and e dehydration of the iodic acid. The product is pure white, s practically 100% of the oxidising value, and contains no detectle impurities except traces of water and barium iodate. It is idedly more stable towards heat than iodic anhydride as ordinly prepared, and, therefore, has decided advantages for use in e analysis of small quantities of carbon monoxide in air. The ld of pentoxide is almost theoretical. In the preparation a small xess (3%) of chloric acid is used; this ensures the complete removal the hydrochloric acid formed during the oxidation process, which ierwise would reduce the iodic acid during evaporation. When s small excess of chloric acid is used, the net result of the oxidan is expressed by the equation $I_2 + 2HClO_3 = 2HIO_3 + Cl_2$. The chanism of this reaction undoubtedly does not correspond with

a direct replacement of chlorine by iodine. The chloric acid solution is made by the direct action of sulphuric acid on barium chlorate solution. There is no decomposition of the chloric acid, and the only loss is the small amount of solution absorbed by the barium sulphate. This method of preparation presents no difficulties on the manufacturing scale. J. F. S.

Colloidal Sulphur. PAUL BARY (*Compt. rend.*, 1920, **171**, 433—435).—Colloidal sulphur in the form of a limpid liquid is a hydrophile colloid, capable of absorbing water. This absorption is favoured by the presence in solution of small amounts of salts of univalent metals, whilst it is prevented by the action of salts of bivalent metals. Such colloidal sulphur is not pure sulphur, but a compound containing sulphur in a highly polymerised state. The compounds are easily dissociable, and only exist in aqueous medium in the presence of substances which limit their decomposition. When the swelling of the granules, due to the absorption of water, becomes small, the granules lose their transparency and the liquid becomes milky and loses its stability. W. G.

Freezing Points of Mixtures of Sulphuric and Nitric Acids. W. C. HOLMES (*J. Ind. Eng. Chem.*, 1920, **12**, 781—783).—The freezing points of mixtures of sulphuric and nitric acids containing 0 to 50% of the latter were determined in test-tubes immersed in an insulated bath of ether and carbon dioxide snow, and the results plotted as curves. In the case of mixtures with a total acidity of 100% the freezing point reached a minimum (−18·2°) when 5·4% of nitric acid was present, and a maximum (+2·3°) with 10·8% of nitric acid. The curve closely resembled that of sulphuric acid and water, which reached a minimum (−34°) with 8·4% of water, and a maximum (+8°) with 15·5% of water. It is probable that at the maximum point in the nitric acid mixtures a definite compound, $5H_2SO_4,HNO_3$, is present, whilst the minimum point coincides with a compound of the approximate composition $5H_2SO_4,\frac{1}{2}HNO_3$. In the determinations with mixtures of a total acidity of 95% the freezing point fell to −41·0° with 2·35% of nitric acid, then rose to −11·0° with 9·75%, and fell again to −41·3° with 49·09%. With mixtures of a total acidity of 103% the minimum (−12·3°) was reached with 8·15% of nitric acid and the maximum (+10·5°) with 15·52%. The last two series of results were complicated by the presence of water and sulphur trioxide respectively. C. A. M.

Vapour-pressure Curves of Solid and Liquid Selenium near the Melting Point. L. E. DODD (*J. Amer. Chem. Soc.*, 1920, **42**, 1579—1594).—The sublimation curve for crystalline selenium (hexagonal) has been determined over the temperature range 190—215° by the method of molecular flow. By the same method data for the vaporisation curve for the liquid of vitreous amorphous selenium have been obtained over the temperature range

220—235°. The relation between vapour pressure and temperature for selenium over the temperature range considered and on the basis of a diatomic vapour may be expressed by a simple exponential equation, $p = c_1 \cdot e^{c_2 T}$, where T is the absolute temperature. On the basis of a diatomic vapour the results appear to locate the melting point at 217·4°, and give a pressure value at the melting point of 12·68 bars (0·00954 mm.), and slope values for the p and T curves at the melting point of 1·050 bars/degree (0·000767 mm./degree) for the crystals, and 0·573 bar/degree (0·000431 mm./degree) for the liquid. The slope at the melting point was thus found to be greater for the solid than for the liquid, as required by thermodynamics, and as found for other substances. The difference between the two slopes is 0·477 bar/degree (0·000358 mm./degree) on the basis of a diatomic molecule. From Clapeyron's first latent heat equation, the three latent heats at the melting point were calculated on the basis of a diatomic vapour, as follows: latent heat of vaporisation, 135·5; latent heat of sublimation, 219·4; and latent heat of fusion, 83·9 cal./gram. Since the vapour density at the experimental temperatures is unknown, the three latent heats, as well as the pressure at the melting point, and the slopes of the p and T curves at the melting point, have been calculated on the basis of 4, 6, 8, 10, and 12 atoms per molecule of vapour. The calculated latent heat values vary inversely as these numbers. These results are not out of keeping with the requirements of the Kirchhoff equation, based on thermodynamics, relating vapour pressure and temperature, but they do not give positive evidence that this equation is applicable to selenium, as would be expected from the limited temperature range even if that relation should apply. J. F. S.

Tellurium Nitrite. FELIX VON OEFELE (*Pharm. Zentr.-h.*, 1920, **61**, 491—492).—By the action of nitric acid on tellurium, under certain conditions, namely, using large quantities of material and a high column of liquid (not less than 50 cm.), tellurium nitrite was obtained as a flesh-coloured precipitate, which could be dried at 100° without decomposition. At higher temperatures it decomposes, leaving a residue of yellow tellurium dioxide. E. H. R.

Rutherford's Experiments on the Subdivision of the Nitrogen Nucleus. W. LENZ (*Naturwiss.*, 1920, **8**, 393; from *Chem. Zentr.*, 1920, iii, 300).—The priority in the explanation of the deficit in the atomic weight by the theory of the lag of energy should be ascribed to Swinne, and not, as previously (this vol., ii, 427), to Harkins and Wilson. H. W.

Determination of the Electrolytic Potential and Overvoltage of Arsenic. VINCENT B. MARQUIS (*J. Amer. Chem. Soc.*, 1920, **42**, 1569—1573).—The normal potential of an arsenic electrode has been calculated from *E.M.F.* measurements of cells of the type Hg,HgCl | LiCl in absolute alcohol‖$AsCl_3$ (0·176*M*) in

absolute alcohol|As. This cell had an *E.M.F.* of 0·153 volt, which, making use of the Rideal and Roderburg method of calculation, is equivalent to 0·040 volt for the arsenic–alcohol potential and 0·111 volt for the arsenic–water potential. From this, the electrode potential, 0·138 volt, is obtained, which places arsenic between hydrogen and copper in the electrode series. The molecular conductivity of arsenic trichloride in alcohol has been determined at 20°, and concentration–conductivity curves drawn. The dissociation of arsenic trichloride in alcohol solution is 20·6% in 0·176*M*-solution. Conductivity determinations also show that there is no appreciable hydrolysis of arsenic trichloride in alcohol solution, but that there is a slight combination with the solvent. The hydrogen overvoltage on arsenic electrodes has been determined by both the open-circuit and closed-circuit methods. The former method gives a value 0·379 volt and the latter 0·478 volt.

J. F. S.

A Decolorising Carbon. JOSEPH C. BOCK (*J. Amer. Chem. Soc.*, 1920, **42**, 1564—1569).—The decolorising action of a vegetable carbon, sold under the name Norit, on biological fluids has been investigated. Norit is found to extract uric acid completely from urine; creatinine is extracted to a large extent, carbamide, total nitrogen and phosphates are removed to a considerable extent, and ammonia–nitrogen, chlorides and dextrose are slightly removed. Bouillon cultures, on shaking with norit for a few seconds and subsequently keeping in contact for three to four minutes, showed a marked decrease in the number of bacteria. Freundlich's simple adsorption formula holds exactly for the adsorption of total nitrogen and creatinine, and probably holds for dextrose. When several substances are present in a given solution, each one of them is adsorbed less than when they are present separately. Thus urine containing 1·77% of dextrose loses no sugar on treatment with norit, whereas a 0·77% aqueous solution of dextrose loses 16·88% of its sugar after the same treatment. Lactose is removed from milk by norit. Washed norit (ash, 2·18%) is more efficient than commercial norit (ash, 5·13%) as an adsorbent.

J. F. S.

The Strength of Aqueous Carbonic Acid Solutions at High Pressures. OTTO HÄHNEL (*Centr. Min.*, 1920, 25—32).—Experiments were made to determine the solubility of carbon dioxide in water at higher pressures, and the electrical conductivity of the solutions. The solutions were prepared by saturating water with carbon dioxide in an autoclave of large capacity. When the pressure had been measured, a quantity of the saturated solution was removed to a special eudiometer, and the excess of gas allowed to escape from the solution at atmospheric pressure, the volume of gas and water being then measured. Determinations were made at 0° at pressures up to 38 atm. and at 15° up to 52 atm. At 0° and 38 atm., a saturated solution contains 7·44% by weight of carbon dioxide, and at 15° and 52 atm., 5·44%. Henry's law

is not obeyed, for the rate of increase in solubility diminishes with increasing pressure. The electrical conductivity of the solutions is very low; thus, a 2·99% solution, at 15° and 20 atm., has a conductivity only half that of a 0·3% solution of acetic acid. It has been shown, however, by Thiel and Strohecker (A., 1914, ii, 361) that in a 0·038% solution of carbon dioxide at 4°, only 0·56% exists in the hydrated form, as H_2CO_3. If the same holds true at higher concentrations and pressures, the true concentration of carbonic acid in a saturated solution at, say, 15° and 52 atm., is 0·027%, and its conductivity, $1·98 \times 10^4$, is of the same order as that of formic acid at a similar concentration. Carbon dioxide must, then, be classed with the stronger acids, a conclusion which accords fully with the known activity of the acid in rock formation and degradation. E. H. R.

Preparation of Thiocarbonyl Tetrachloride. PERCY FARADAY FRANKLAND, FREDERICK CHALLENGER, and DOROTHY WEBSTER (*J. Soc. Chem. Ind.*, 1920, **39**, 256—257T).—For the preparation of thiocarbonyl tetrachloride on a large scale, 4 grams of iodine are added to 2 kilos. of carbon disulphide dried over calcium chloride, dry chlorine is passed in, the temperature not being allowed to exceed 20°, until the increase in weight corresponds with the absorption of five atomic proportions of chlorine, when the reaction mixture is run, in a thin stream, into hot water through which steam is being blown. Sulphur chloride is thus decomposed, and thiocarbonyl tetrachloride distils over. The latter is again distilled with steam, then dried over calcium chloride, and fractionally distilled until the temperature reaches 140°. The residue in the flask is the required thiocarbonyl tetrachloride, and by this process a 60% yield may be obtained. It should be noted that thiocarbonyl tetrachloride is completely decomposed by contact with metallic iron at the ordinary temperature. W. G.

Behaviour of Concentrated Alkali Chloride Solutions in Presence of Alkali Hydroxides. CH. CHOROWER (*Zeitsch. angew. Chem.*, 1920, **33**, 201—203).—The author has investigated the solubility of alkali chlorides in liquors derived from the treatment of vinasses ash with lime and barium hydroxide. The composition of an experimental liquor was: Cl, 3·559; OH, 0·9278; K, 4·792; Na, 0·933; S, 0·0594; SO_4, 0·0321; CO_3, 0·0705%. The liquor was evaporated in quantities of 4 litres, and boiling-point determinations were made at various stages when deposition of salts ceased. The density was then determined in a modified pyknometer, and the samples analysed. Six samples tested from quantities of 15, 20, 25, 35, 41, and 48 litres, with boiling points 110°, 111°, 112°, 115°, 116°, and 118°, showed increasing densities from 1·295 to 1·370. The chlorine ions diminished from 12·58 to 7·661, and potassium ions remained nearly constant at approximately 17, but all the other ions gave progressively rising values. The author discusses the phenomena by the application of the theory of mass action and of the phase rule. W. J. W.

Oxidation of Potassium Plumbite to Plumbate by means of an Alternating Current. FRANZ JIRSA (*Zeitsch. physikal. Chem.*, 1920, **94**, 1—5).—The electrolysis of a solution (*N*) of potassium hydroxide between lead electrodes by means of an alternating current of 49 periods brings about the formation of potassium plumbite as the only product. It is shown that the plumbite may be electrolytically oxidised to plumbate if electrodes of suitable metals are used. The metals copper, silver, gold, cadmium, magnesium, mercury, nickel, iron, platinum, and palladium when used as electrodes with alternating current effect the oxidisation but no oxidation occurs when lead, bismuth, cobalt, thallium, or carbon is used. The nature of the electrode is also determinative of the product of the oxidation; under the same conditions (40 grams of potassium hydroxide and 4·5 grams of lead oxide per litre) with palladium electrodes, yellow lead sesquioxide separates and lead metaplumbate is formed, whilst with nickel or iron electrodes a dark brown powder separates, which is the dioxide, and the yellow plumbate is not formed. It is shown also that, even with electrodes which are capable of effecting oxidation, oxidation does not always take place; under certain conditions, reduction, or even oxidation and reduction, may occur. The disintegration of the electrodes is an accelerating factor of the reaction. J. F. S.

Sodium Phosphide. E. TOMKINSON and G. BARKER (*Chem. News*, 1920, **121**, 104—105, 177).—When sodium is heated with red phosphorus, amongst other products, a grey mass is obtained, which is acted on violently by water, giving spontaneously inflammable hydrogen phosphide. With yellow phosphorus under suitable conditions, a white, crystalline product is obtained. W. G.

The Third and the Fourth Dissociation Constants of Pyrophosphoric Acid and the Examination of the Purity of Sodium Pyrophosphate. I. M. KOLTHOFF (*Pharm. Weekblad*, 1920, **57**, 474—481).—The hydrogen-ion concentration of dilute solutions of sodium pyrophosphate was determined colorimetrically by comparing the colour change of thymolphthalein in these solutions and in mixtures of carbonate and hydrogen carbonate solutions of known p_H value. From the results, a mean value of $4·6 \times 10^{-9}$ for the fourth dissociation constant was calculated. Further measurements with mixtures of pyrophosphate and small quantities of hydrochloric acid, so as to give the ion HP_2O_7''' in presence of P_2O_7'''', led to the result $K_4 = 3·6 \times 10^{-9}$, with certain assumptions as to the degree of dissociation of the solution. The third dissociation constant was determined in a similar way by measurements in mixed solutions of $Na_3HP_2O_7$ and $Na_2H_2P_2O_7$, the value $K_3 = 7·6 \times 10^{-7}$ being obtained. W. S. M.

Metastability of the Metals as a Consequence of Allotropy and its Significance for Chemistry, Physics, and Technics. IV. ERNST COHEN and H. B. BRUINS (*Zeitsch. physikal. Chem.* 1920, **94**, 443—449. Compare A., 1914, ii, 52, 202, 332, 652, 799; 1915, ii, 52, 83, 417, 471, 565, 634; 1916, ii, 183).—A repetition

of earlier experiments in which a change in density of silver and cadmium was found after keeping under solutions. This change has been attributed to the adsorption of water or solution. The present experiments were undertaken to ascertain whether or no the metal does contain water after the treatment. The results show that whilst water is contained in the metals to the extent of 0·1—0·001%, the amount is so small as to be without effect on the density, and consequently can play no part in the changes previously observed. J. F. S.

Binary System Åkermanite–Gehlenite. J. B. FERGUSON and A. F. BUDDINGTON (*Amer. J. Sci.*, 1920, [iv], **50**, 131—140. Compare Ferguson and Merwin, A., 1919, ii, 459).—The binary system åkermanite ($2CaO,MgO,2SiO_2$)-gehlenite ($2CaO,Al_2O_3,SiO_2$) has been studied by the quenching method, and the curves of the solid and the liquid phases constructed. The system is found to consist of a complete series of solid solutions with a minimum melting point, 1388°, 70° below that of åkermanite (1458°). The refractive index and general optical characteristics have been determined for the intermediate compositions, and are found to be a continuous function of the composition. Crystals of a certain intermediate mixture are isotropic for sodium light, and constitute a transition phase from crystals of positive optical character to those of negative optical character. Zoned crystals showing material of both positive and negative optical character in the same crystal were obtained. These are analogous, in this respect, to certain natural melilite crystals which have been previously described. The densities of crystals of åkermanite, gehlenite, and several intermediate mixtures have been determined and found to confirm the isomorphous character of the system. Åkermanite was found to show the unusual feature of its glass having a greater density (2·955) than the corresponding crystals (2·944) at 25°. J. F. S.

Piezo-chemical Studies. XVI. Experimental Proof of Braun's Law by an Electrical Method. ERNST COHEN, J. W. G. HETTERSCHIJ, and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1920, **94**, 210—232. Compare A., 1919, ii, 321).—Braun's law has been experimentally examined for the case of cadmium iodide by the electrical method of Cohen and Sinnige (A., 1909, ii, 981), and it is shown that within the limits of the experimental error this law accurately represents the experimentally found facts. To arrive at this conclusion the following data have been obtained for cadmium iodide: temperature-coefficient of the solubility, $(\partial x/\partial T)_{30\cdot0°} = +0·1003 \pm 0·001$ gram per 100-gram solution/degree; pressure-coefficient of the solubility, $(\partial x/\partial \pi)_{30\cdot0°} = -0·00390 \pm 0·0002$%/atm.; the fictitious volume change, $\Delta V = 0·0191 \pm 0·0003$ c.c./gram, and the fictitious heat of solution, $Q_{30\cdot0°} = 3·71 \pm 0·07$ gram-cal./gram. Substituting the first three of the above quantities in Braun's equation, the value of Q is found to be $3·60 \pm 0·19$ gram-cal./gram. The determination of the pressure-coefficient of the solu-

bility indicates that this factor may no longer be regarded as negligibly small. J. F. S.

Metastability of Elements and Compounds as a Consequence of Enantiotropy or Monotropy. III. Cadmium Iodide. ERNST COHEN and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1920, **94**, 471—481. Compare this vol., ii, 620).—Cadmium iodide has been carefully examined, and it is shown that at temperatures between that of the melting point and ordinary temperature, it exists in two modifications which stand to one another in monotropic relations. Cadmium iodide obtained by crystallisation from solution or by sublimation is a mixture of α- and β-forms in unknown quantities. The physical properties of cadmium iodide hitherto recorded, except those recorded by Cohen, Hetterschij, and Moesveld (preceding abstract), refer to a mixture of the α- and β-forms of unknown composition. J. F. S.

Melting Points and Thermoelectric Behaviour of Lead Isotopes. THEODORE W. RICHARDS and NORRIS F. HALL (*J. Amer. Chem. Soc.*, 1920, **42**, 1550—1556).—The melting points of two isotopic varieties of lead, which differed by 0·8 in atomic weight, have been determined and found to differ by not more than 0·05°. From this result it may be assumed that the other kinds of lead not only have very nearly the same melting point, but also, since the sample consisting chiefly of lighter isotopes doubtless contained ordinary lead, that they mix or, better, mutually dissolve without affecting the melting point. The Seebeck thermoelectric effect produced at the junction of the two kinds of lead was determined and found to be zero. (See also A., 1916, ii, 250.) J. F. S.

Disglomeration: a New Mode of Transformation of Solidified Metals. A. THIEL (*Sitzungsber. Ges. gesamt. Naturwiss. Marburg*, 1920, i, 1—17; from *Chem. Zentr.*, 1920, iii, 227).—The allotropy of lead does not play any part in the transformation of lead according to Heller's experiments (A., 1915, ii, 634; compare also Cohen and Heldermann, A., 1915, ii, 456). Disglomeration (disintegration in consequence of the solution of the eutectic formed by lead and its impurities and located between the lead crystals) is a consequence of the chemical action of the dissolved nitrate and formation of lead nitrite. Disglomeration only occurs with solidified metals (copper in addition to lead). Formation of the lead tree is only observed when local, short-circuited, ionic concentration cells are developed. All types of lead which separate as the lead tree are crystallographically identical with that which has crystallised from the molten metal; the earlier explanation of the phenomenon as being due to allotropy is therefore excluded.

H. W.

Rate of Dissolution of Metallic Copper in Aqueous Ammonia. EIICHI YAMASAKI (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, **9**, 169—220).—The copper was vigorously rotated with a con-

stant velocity in ammonium hydroxide, and a steady current of air passed through. Two chemical actions take place in the solution, the electrolytic dissociation of the copper and the autocatalytic reaction of cuprammonium compound in solution. The velocity of the former increases proportionally to the square root of concentration of free oxygen, and the rate of the latter to that of the cuprammonium compound. The total velocity is independent of the concentration of free ammonia and the nature of the anions. The dissolution velocity increases regularly to a maximum and then decreases again. The maximum is attained at a concentration of cuprammonium hydroxide, which is practically proportional to the concentration of free ammonia. The range of solution of copper is increased by the presence of an ammonium salt. A mathematical formula is obtained which represents the course of the reaction with sufficient accuracy. The velocity of dissolution is found to be roughly proportional to a two-thirds power of the rate of stirring. The temperature-coefficient is only 1·15, so that probably the velocity of reaction is chiefly determined by that of diffusion. Diffused daylight has no effect on the velocity. With the addition of hydroxylamine, dissolution takes place very slowly, probably due to the checking of the autocatalytic action of the dissolved copper. Sodium oleate has a retarding effect, and amalgamation considerably reduces the velocity. The effect of carbon monoxide is slight, but hydrogen peroxide increases the initial velocity of dissolution. The best conditions for the preparation of the solution of cuprammonium hydroxide are discussed on the basis of the present investigation in view of its importance in the manufacture of artificial silk. T. H. B.

Similarity in Micrographic Appearance Existing at Different States between Iron–Carbon Alloys (Steels), Copper–Tin Alloys (Bronzes with Tin), Copper–Zinc Alloys (Brasses), and Copper–Aluminium Alloys (Bronzes with Aluminium). A. Portevin (*Compt. rend.*, 1920, **171**, 350—353).—In the case of copper–tin and copper–aluminium alloys the austenitic, martensitic, and troostitic states have previously been observed, as well as the two aspects of the eutectoid. For copper–zinc alloys the austenitic and troostitic states have been observed, and the author has now obtained microphotographs showing first the eutectoid resolved during cooling, and secondly the martensitic state for these alloys. W. G.

Chemical and Electrochemical Properties of Copper–Zinc Alloys Prepared by Melting or by Electrochemical Processes. Franz Sauerwald (*Zeitsch. anorg. Chem.*, 1920, **111**, 243—279).—An account is given of the action of various reagents, such as solutions of cadmium sulphate, copper sulphate, sulphuric acid, hydrochloric acid, thallous sulphate, lead chloride, lead nitrate, and alkali sulphides, on alloys of zinc and copper prepared by various methods and of varying composition. The *E.M.F.* of alloys (100—18·4% Cu) against a solution of zinc chloride has also been measured, and the change with temperature ascertained. It is

shown that the behaviour of zinc–copper alloys is governed by the two factors which determine the chemical and electrochemical behaviour of mixed crystals, namely, the nature of the partition of the components and the mobility of the atoms in the crystal lattice. It is shown that the mixed crystals, obtained by melting, with ordered partition corresponding with the equilibrium conditions, have chemical and electrochemical properties at the ordinary temperature which to a large extent are independent of the concentration. This is to be attributed to the protecting action of the copper. The properties change sharply and suddenly only on the appearance of a new crystal form with a different lattice, whereby *in the case of copper saturated with γ-crystals, the properties of the compound* Cu_2Zn_3 *were observed.* At 380°, where a considerable mobility of the atoms in the lattice exists, the electrochemical properties of the mixed crystals are dependent on the concentration, since the copper is no longer able to afford a protecting action. In the case of unordered atom partition, which is obtained by electrolytic deposition at the ordinary temperatures, the copper is only able to afford a very slight protecting action to the zinc. From this the simple relationship follows that the logarithm of the solution pressure of the zinc in alloys with unordered partition is proportional to the number of unprotected zinc atoms. The atom partition brought about by electrolysis is to a large extent dependent on the temperature, for it is shown that by the electrolysis of molten salts at 300° an alloy is obtained in which the atom partition is very nearly that of the equilibrium condition. J. F. S.

Topochemical Reactions. Formation and Behaviour of Copper Hydroxide. V. KOHLSCHÜTTER and J. L. TÜSCHER (*Zeitsch. anorg. Chem.*, 1920, **111**, 193—236).—A topochemical reaction is defined as one which depends on the relative position in space of the reacting groups or molecules. The present paper gives a long account of the various methods of preparation of copper hydroxide and the properties of the various products. In particular the loss of water from the hydroxide to form oxide and partly dehydrated hydroxides is considered. Four means of dehydrating copper hydroxide are considered: (i) thermal separation of water $Cu(OH)_2 \longrightarrow CuO + H_2O$; (ii) separation of water by osmotic pressure owing to the evaporation of the surrounding liquid; (iii) endosmotic drying of the hydrated compound on an anode; and (iv) water separation by internal neutralisation, due to amphoteric ionisation. The authors are of the opinion that the dehydration of copper hydroxide takes place according to the last-named method. The process is represented by the equations $Cu(OH)_2 \rightleftharpoons Cu^{\cdot\cdot} + 2OH'$; $Cu(OH)_2 \rightleftharpoons CuO_2'' + 2H^{\cdot}$; $HO' + H^{\cdot} \rightleftharpoons H_2O$; and $CuO_2'' + Cu^{\cdot\cdot} = 2CuO$. J. F. S.

The Electro-affinity of Aluminium. III. The Acidity and Constitution of Aluminic Acid. JAROSLAV HEYROVSKÝ (T., 1920, **117**, 1013—1025).

Hydrates of Aluminium Nitrate. KENZO INAMURA (*J. Tokyo Chem. Soc.*, 1920, **41**, 1—8).—Mixtures of aluminium nitrate ($18H_2O$), nitric acid, and water in various proportions are left for one to two days at 25°. After the equilibrium is established, the solution is separated from the residue, and aluminium, nitric acid, and water are estimated in the two fractions. The results are given in two tables and two curves, which show that in proper concentrations of nitric acid, at 25°, the nitrate produces three hydrates containing 18, 16, and 12 H_2O respectively. The first hydrate is most stable in 73% (D^{15} 1·435) or a weaker nitric acid, the next hydrate in 73—81% (D^{15} 1·1435—1·1463), and the last in nitric acid stronger than 81%. CHEMICAL ABSTRACTS.

Phosphomolybdic and Phosphotungstic Acids and Allied Substances. HSEIN WU (*J. Biol. Chem.*, 1920, **43**, 189—220).—The somewhat confused literature on these acids is reviewed. There are two series of these complex acids, in which the ratios $P_2O_5 : XO_3$ are 1 : 18 and 1 : 24 respectively, and simple methods for their preparation are given.

There appear to be two isomeric forms of the phosphotungstic acid, $P_2O_5.18WO_3$, and there are a number of complex acids containing both molybdenum and tungsten which belong to both the 18- and the 24-series.

On moderate reduction, the complex acids give rise to a number of new complex acids containing lower oxides of molybdenum and tungsten. The value of the complex acids of phosphorus and tungsten or molybdenum as analytical reagents is fully treated.

J. C. D.

An Approximate Determination of the Melting-point Diagram of the System Zirconia–Silica. E. W. WASHBURN and E. E. LIBMAN (*J. Amer. Ceram. Soc.*, 1920, **3**, 634—640).—The melting points of mixtures of zirconia and silica were determined by heating one end of a small rod, 5 cm. long and 0·3 cm. in diameter, in an oxy-acetylene flame and measuring the temperature of the droplets of fused material with an optical pyrometer. Temperature readings could be duplicated to about ±100°. By this means, it was found that the melting point of pure zirconia is about 2700°, and that of natural zircon about 2300°. A eutectic between ZrO_2 and $ZrSiO_4$ occurs near 2300°. [See *J. Soc. Chem. Ind.*, 628A.] A. B. S.

Metastability of Elements and Compounds as a Consequence of Enantiotropy or Monotropy. II. Antimony Tri-iodide. ERNST COHEN and H. R. BRUINS (*Zeitsch. physikal. Chem.*, 1920, **94**, 465—470. Compare this vol., ii, 620).—Antimony iodide has been stated by Cooke (*Proc. Amer. Acad.*, 1878, **5**, 1, 72) to belong to the enantiomorphic substances, and to crystallise in red, hexagonal crystals and yellow, rhombic crystals with a transition point at 114°. This change has been carefully

re-examined, and it is shown that antimony iodide is a monotropic substance, and that the temperature 114° found by Cooke was accidental. Antimony iodide prepared by sublimation is a metastable system, which may remain unchanged for long periods even at low temperatures. J. F. S.

Mineralogical Chemistry.

Regular Grouping of Two Minerals in Titaniferous Iron-ores. A. Lacroix (*Compt. rend.*, 1920, **171**, 481—485).—The compound $FeTiO_3$ (corresponding with TiO_2 52·65, FeO 47·35%) is represented most nearly in nature by the mineral crichtonite from Oisans, Isère, and it is proposed to limit this name to such a compound. In most ilmenites, however, the composition is more complex, and was represented by Rammelsberg as $FeTiO_3 + xFe_2O_3$. These two components have been assumed to form an isomorphous mixture (although they do not possess the same degree of symmetry) or to form a solid solution; or, again, the isomorphous mixing of Ti_2O_3 and Fe_2O_3 has been assumed. Specimens of ilmenite from Madagascar, however, show very distinctly a fine, lamellar intergrowth of two minerals (crichtonite and hæmatite) similar to the perthitic intergrowth of the felspars. The layers of hæmatite are attacked by hydrochloric acid, leaving, finally, isolated lamellæ of crichtonite. Analysis by Raoult of a specimen from Andongovato, near Itrongay, gave:

TiO_2.	FeO.	MnO.	MgO.	Fe_2O_3.	Total.	Sp. gr.
27·41	23·99	0·22	0·25	47·95	99·82	4·96

corresponding with hæmatite 47·95 and crichtonite 51·87%. The original ilmenite from the Ilmen Mtns. (containing TiO_2 45—48%) appears to be homogeneous, but the washingtonite variety from Litchfield, Maine (TiO_2 22—24%), shows very distinctly the perthitic intergrowth, whilst in crystals from Snarum, Norway (TiO_2 6—10%), the bands of crichtonite are very thin. The name ilmenite is therefore reserved for the homogeneous types, and washingtonite for those showing the intimate intergrowth of the two minerals. Similar regular intergrowths are also shown by the titaniferous magnetites of Madagascar, the two minerals in this case being magnetite and crichtonite. Layers of needles of brown rutile enclosed parallel to the octahedral planes of the magnetite are shown to be due to the secondary transformation of crichtonite L. J. S.

Blödite and other Minerals of the Saliferous Stratum of Monte Sambuco in the Calascibetta Region (Sicily). F. Millosevich (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 344—347).—Crystals of blödite, some colourless and others red, owing to

iclusions of ferric oxide, occur locally in the deposit of hard salt, onsisting essentially of kieserite and rock-salt, found in the aliferous mass of Monte Sambuco; they belong to the monoclinic stem, $a:b:c=1\cdot34939:1:0\cdot67047$, $\beta=79°21'42''$. The perntage composition:

Na_2O.	MgO.	SO_3.	H_2O.	Insol.	Total.
18·61	12·00	47·41	21·42	0·49	99·83

grees well with the formula $Na_2SO_4,MgSO_4,4H_2O$.

The name blödite has a prior claim to astracanite, which was sed first to indicate the rock, that is, the material forming disnct layers in the saliferous deposits, such as those of the salt kes of the Astracan steppe.

The astracanite mass of the upper gallery of Monte Sambuco ontains many rounded, white nodules, which vary in size (peas o oranges), have a granular, saccharoid structure, deliquesce partly n moist air, contain boric acid, magnesium, and chlorine, and osely resemble the nodules of compact boracite (stassfurtite) ccurring among the carnallite of the Stassfurt deposits.

T. H. P.

Optical Properties of Anthophyllite. N. L. Bowen (*J. Washington Acad. Sci.*, 1920, **10**, 411—414).—A revision of the ptical constants for Penfield's (1890) original material from ranklin, North Carolina (containing SiO_2 57·98, Al_2O_3 0·63, eO+MnO 10·70, MgO 28·69%), gave: $\alpha=1\cdot6195$, $\beta=1\cdot6301$, $=1\cdot6404$, $\gamma-\alpha=0\cdot0209$, $2V=88°46'$ (Na). For the artificial agnesium metasilicate (kupfferite) described by Allen, Wright, nd Clement (1906), revised values are: $\alpha=1\cdot584$, $\gamma=1\cdot597$. In nthophyllite, the refractive indices increase regularly with the ercentage of ferrous oxide. L. J. S.

The Existence in Madagascar of a Silicate of Scandium nd Yttrium, Thortveitite. A. Lacroix (*Compt. rend.*, 1920, **71**, 421—423).—Thortveitite has been found in the pegmatite t Befanamo, in Madagascar, and resembles in its properties the ame mineral previously discovered in Iveland, Norway, and escribed by Schetelig (A., 1912, ii, 56). W. G.

Analytical Chemistry.

Theory of Indicators Used in Acidimetry. Gustav F. Hüttig (*Zeitsch. physikal. Chem.*, 1920, **95**, 280—284).—A heoretical paper in which the results of Wegscheider (A., 1916, ., 108) and the previous paper of the author (A., 1914, ii, 597) re discussed, and the optical and electrochemical behaviour of ndicators further developed. J. F. S.

A Polychromatic Indicator. JAMES MOIR (*J. S. African ssoc. Anal. Chem.*, 1920, **3**, 6—8).—The indicator is 3 : 3-dihydr-ybenzaurine-2-sulphonic acid, and is prepared by condensing techol with *o*-sulphobenzoic acid. It exhibits the following nge of colours in acid and alkaline solutions: strong acid, urplish-pink; dilute acid (*N*/10), salmon-orange; more dilute acid /40), yellow; neutral solution (or, more exactly, $p_H = 6{\cdot}5$), prac-ally colourless; dilute alkali ($p_H = 7{\cdot}5$), violet; stronger alkali $_H = 10$), indigo-blue; concentrated alkali, grass-green.

W. P. S.

Use of Potassium Hydrogen Phthalate as a Standard in lkalimetry. F. D. DODGE (*J. Amer. Chem. Soc.*, 1920, **42**, 55—1656. Compare Hendrixson, this vol., ii, 382).—In the pre-ration of potassium hydrogen phthalate for use as a standard in calimetry, it is advisable to crystallise above 20°, because in this y the formation of a more acid salt, $2KHC_8H_4O_4,C_8H_6O_4$, is ectually prevented.

J. F. S.

Influence of Atmospheric Carbon Dioxide on Alkali-etric Titrations, using Phenolphthalein as Indicator. BRUHNS (*Zeitsch. Zuckerind. Čechoslav.*, 1920, **44**, 331—335).—mparative titrations with *N*/100-sodium hydroxide and hydro-loric acid solutions, using phenolphthalein and methyl-orange as licators, showed that, with the former indicator, less acid was quired to neutralise a given quantity of the alkali than when ethyl-orange was employed. The difference was about 0·5 c.c. r 10 c.c. of acid used, and was due to carbon dioxide absorbed om the atmosphere during the titration.

W. P. S.

The Significance of the Dissociation Constant in the lentification of Acids and the Detection of Impurities herein. I. M. KOLTHOFF (*Pharm. Weekblad*, 1920, **57**, 514—518). -The dissociation constant of weak organic acids may be used for eir characterisation. This may be conveniently determined by timating the hydrogen-ion concentration at a given dilution by mparing the colour change of the same indicator in the solution id in a standard solution of known ion concentration. Such andard solutions are represented by very dilute hydrochloric acid by mixtures of potassium hydrogen phthalate with hydrochloric id or sodium hydroxide. A selection of suitable indicators is ven for various weak acids. The mineral acid or base in a solu-on of an organic acid may be estimated by measuring the change the p_H value of the solution consequent on the addition of a iown small quantity of mineral acid or base. The method of lculation is exemplified in the case of tartaric acid.

W. S. M.

The Neutralisation of Weak Acids with Weak Bases and ie Examination of the Purity of Ammonium Salts of 'eak Acids. I. M. KOLTHOFF (*Pharm. Weekblad*, 1920, **57**, 17—796).—The exact titration of a weak acid with a weak base

is practicable if a suitable indicator is chosen, the choice of the latter being determined by the hydrogen-ion concentration of the resulting salt solution; that is, the p_H value to which it is desired to titrate must be determined beforehand. An expression,

$$[H^{\cdot}] = \sqrt{K_{H_2O} . K_{HA}/K_{BOH}},$$

is derived giving the hydrogen-ion concentration in terms of the dissociation constants of the weak acid, the weak base, and water. With the help of this equation, the $[H^{\cdot}]$ for mixtures of acid and base is calculated, and the neutralisation curve constructed by plotting $p_{H^{\cdot}}$ against the composition of the mixture. This curve shows an inflexion for the $p_{H^{\cdot}}$ corresponding with the neutral point. An indicator is then chosen for which the $p_{H^{\cdot}}$ in the range of colour change is approximately equal to the calculated value. For example, in the titration of ammonium acetate ($p_{H^{\cdot}} = 7.1$), neutral-red with a range $p_{H^{\cdot}} = 6.8$ to $p_{H^{\cdot}} = 8.0$ is chosen. Satisfactory results were obtained for ammonia and oxalic acid (neutral-red), ammonia and succinic acid (neutral-red), ammonia and formic acid (methyl-red), and ammonia and salicylic acid (methyl-red). A method for testing the purity of ammonium salts of weak acids is indicated. W. S. M.

Liquid Ammonia–Sodium Method for the Estimation of Halogens in Organic Compounds. F. B. DAINS and R. Q. BREWSTER (*J. Amer. Chem. Soc.*, 1920, **42**, 1573—1579).—It has been pointed out by Clifford (A., 1919, ii, 423) that in some cases there is a considerable formation of cyanide in the estimation of halogens by the liquid ammonia–sodium process. With the object of ascertaining to what extent and in what circumstances this occurs, the reaction has been carried out with 123 organic compounds, some of which did not contain any halogen, and the resulting solutions tested for cyanide. In most cases there was no cyanide present, but in a few, such as chloroform, bromoform, chloral hydrate, and bromal hydrate, considerable quantities of sodium cyanide are formed, according to the equation $CHBr_3 + NH_3 = HCN + 3HBr$, whilst acetonitrile, phenylacetonitrile, and cyanoacetic ester also yield cyanide by direct separation. Cyanides are also formed by ethylidene chloride, tetrachloroethylene, and tetrachloroethane. In all these cases, the estimation of the halogen can be carried out by the modification of the method put forward by Clifford (*loc. cit.*). A large number of estimations are recorded which show that this method of analysis is trustworthy. Attempts to use the liquid ammonia–sodium method for the estimation of cyanogen in organic compounds have shown the unsuitability of the process for this purpose, chiefly because of the formation of amines, according to the equation $CH_3{\cdot}CN + 4NH_3 + 4Na = C_2H_5{\cdot}NH_2 + 4NaNH_2$. It is a remarkable fact that iodoform does not give cyanide by this process. J. F. S.

Use of Alundum Filtering Crucibles. D. T. ENGLIS (*J. Ind. Eng. Chem.*, 1920, **12**, 799—800).—Soluble salts may be removed from the upper part of an alundum crucible in which a

precipitate has been collected by supporting the crucible in suitable holder in an ordinary glass funnel, covering the top the crucible with a rubber stopper, applying suction to the ste of the funnel, and pouring the wash-water into the top of tl latter. W. P. S.

Chemical Analysis with Membrane Filters. L. MOSER a KITTL (*Chem. Zeit.*, 1920, **44**, 637—638).—Whilst membra filters (A., 1918, ii, 307) are useful for the collection of colloid precipitates, their use in quantitative analysis is limited by tl fact that, in spite of the smooth surface of the filter, it is impossib to remove the whole of the precipitate for weighing, since partic of the precipitate appear to become embedded in the membra (compare also A., 1919, ii, 520). W. P. S.

Wash-bottle for giving a Continuous Stream of Wate HANS KLEIN (*Chem. Zeit.*, 1920, **44**, 599).—The mouthpiece an ordinary wash-bottle is fitted with a length of rubber tubi which may be closed with a spring clip, the "bow" of the cl fitting round the cork of the bottle. The bottle is used in th usual way, the clip being closed when there is a sufficient pressu in the bottle and opened to stop the flow of water from the jet. W. P. S.

Apparatus for Evolution Methods of Analysis. E. I DOVEY (*Analyst*, 1920, **45**, 330—332).—An apparatus suitable f the estimation of available oxygen in manganese dioxide, sulphur i steel, etc., consists of a reaction flask, the delivery tube of whic extends into a test-tube containing the solution for absorbing th evolved gas; the test-tube may in turn be connected with a sma U-tube containing a small quantity of absorbing solution. A tub extends to the bottom of the reaction flask, and admits air whe the pressure in the flask decreases from any cause. Another appara tus, which may be used for absorbing carbon dioxide in the estim tion of carbon in steel by the wet combustion method, consists of reaction flask fitted with a reflux apparatus; the long stem of tapped funnel extends through the inner tube of the reflux appar tus to the bottom of the flask. The carbon dioxide is conduct from the top of the reflux apparatus to the bottom of a buret containing barium hydroxide solution and in which a rod fitted wi discs is placed (an efficient absorption apparatus). The top of th burette is connected with an aspirator. When the absorption the carbon dioxide is complete, the jet of the burette is pass through a rubber stopper closing a filter tube, the contents of th burette are filtered, and the barium carbonate washed. W. P. S.

The Calibration, Accuracy, and Use of Gas Meter AUGUST KROGH (*Biochem. J.*, 1920, **14**, 282—289).—A larg recording spirometer for calibrating gas meters is described. Whe properly handled, wet gas meters are instruments of precisio Motor-driven wet meters acting as pumps and having a consta

ater level maintained by a slow current of water are accurate to ss than 0·1% at all rates below 1 revolution per minute. When alibrated for more rapid rates, they can be used with almost the ume accuracy at rates up to 3 revolutions per minute. The volume er revolution decreases with increasing rate. In wet meters with a onstant quantity of water the volume per revolution increases with icreasing rate, but can be determined with equal accuracy.

Dry gas meters are on the whole less accurate than wet meters, nd when arranged to show the volumes directly in litres their indiations are often very inaccurate and cannot be calibrated. They hould be arranged to count revolutions. Gas volumes representing actions of a complete revolution are generally very inaccurately idicated, but the volume corresponding with a whole revolution is practically constant quantity. Varying rates may cause variations n the volume registered, but at practicable rates the variation is sually within 1%. The calibration of a dry meter changes with ge. J. C. D.

Estimation of Iodine in Connexion with Studies in 'hyroid Activity. III. E. C. KENDALL [with AVRINA PUGH, '. S. RICHARDSON and C. FORBES] (*J. Biol. Chem.*, 1920, **43**, 49—159).—The method previously described (A., 1912, ii, 864; 914, ii, 815) is modified to render it applicable to the estimation f iodine in blood and tissue. The modifications consist mainly of he removal of oxidising substances from the phosphoric acid emloyed by reduction with aluminium, the adjustment of the acidity uring boiling, and the use of a small piece of hard coal to facilitate he removal of the added bromine. J. C. D.

Estimation of Iodine in Blood and in Animal Tissues. V. E. C. KENDALL and F. S. RICHARDSON (*J. Biol. Chem.*, 1920, **3**, 161—170).—The application of the method described in the revious paper, to the analysis of tissues poor in iodine, such as blood, as not practicable until a method of destroying large amounts of rganic matter without loss of iodine had been evolved. Destrucive distillation of the tissue with about 3% by weight of sodium ydroxide at 300—400° destroys much of the organic matter withut appreciable loss of iodine. The charred residue is then xtracted with water, and much of the residual organic matter in he brown solution is removed by treatment with barium hydroxide. second fusion in a small crucible, after evaporation to dryness, ffects complete incineration. Special forms of heating chambers for he crucibles are described. J. C. D.

Volumetric Estimation of Hydrosulphides in the 'resence of Sulphides, Thiosulphates, and Sulphites. A. VÖBER (*Chem. Zeit.*, 1920, **44**, 601).—Sodium hydrosulphide when reated with excess of mercuric chloride solution yields free hydrohloric acid according to the equation $2NaHS + 3HgCl_2 = 2NaCl + Hg_3S_2Cl_2 + 2HCl$; under similar conditions sodium thiosulphate gives

free sulphuric acid (compare Sander, A., 1916, ii, 111), whil sodium sulphide gives a neutral solution. By titrating the acidit produced by mercuric chloride before and after the test solution ha been treated with zinc carbonate, the quantities of thiosulphate an hydrogen sulphide may be estimated; the other constituents may b estimated as described by Sander (*loc. cit.*). W. P. S.

Estimation of Selenium [in Organic Compounds]. Fri WREDE (*Zeitsch. physiol. Chem.*, 1920, **109**, 272—275).—Th method here described is based on that given by Pregl for the est mation of sulphuric acid ("Die quantitative organische Mikro analyse," 1917, 122), and consists in burning the substance in tube in oxygen in presence of platinum as catalyst and titratin the selenious acid formed with centinormal sodium hydroxide sol tion, sodium hydrogen selenite being neutral to methyl-orange [See also *J. Soc. Chem. Ind.*, 1920, October.] T. H. P.

Estimation of Ammonia in Urine [with Remarks on th Technique of the Micro-Kjeldahl Method]. LUDWIG PINCUSSOH (*Biochem. Zeitsch.*, 1919, **99**, 267—276).—The urine is heated i the distilling flask of a modified micro-Kjeldahl apparatus at 45 with sodium carbonate, and the ammonia is aspirated into a receive containing standard sulphuric acid and is estimated either by titra tion or colorimetrically. The time taken for the distillation of th ammonia (ten minutes) is not sufficiently long to allow the conve sion of the urea into ammonia. S. S. Z.

Estimation of Phosphorus in Small Quantities of Bloo and Blood-serum. POUL IVERSEN (*Biochem. Zeitsch.*, 1920, **10** 22—29).—The author describes a modification of Neumann method (A., 1903, ii, 243), which admits of the estimation of pho phorus in small volumes of blood or serum (compare Feigl, A., 191 i, 138). T. H. P.

Titrimetric Estimation of Phosphoric Acid I Neumann's Method. POUL IVERSEN (*Biochem. Zeitsch.*, 19 **104**, 15—21).—In this method for estimating phosphorus in orga substrata (A., 1903, ii, 243), the organic matter is destroyed means of sulphuric and nitric acids, the phosphate formed preci tated as ammonium phosphomolybdate, and the latter washed wi ice-cold water, which is filtered; the filter and precipitate are th treated with slightly more $N/2$-sodium hydroxide solution than necessary to dissolve the precipitate, and the ammonia thus liberat boiled off and estimated by titration: (c.c. of $N/2$-NaOH) 0·5539 = amount of phosphorus in milligrams. Gregersen (A., 190 ii, 64) found it to be necessary to over-titrate with 0·5—1 c.c. acid and to boil to expel carbon dioxide. Heubner (A., 191 ii, 675), who dissolves the precipitate on the filter by means of t standard sodium hydroxide solution, gives, however, a higher fact than the above, namely, 0·57. The author shows that Gregerse

modification gives good results, provided that the excess of $N/2$-NaOH taken is at most 4 c.c., and is subject to no systematic error; the mean value of the factor is found, from twenty-five analyses, to be 0·5526 (compare Kleinmann, this vol., ii, 634).

T. H. P.

Estimation of Phosphoric Acid in Phosphates of the Heavy Metals. F. SEELIGMANN (*Chem. Zeit.*, 1920, **44**, 599).—The phosphate (10 grams) is heated at 90—95° for fifteen minutes with 12 grams of sodium hydroxide solution (D 1·383), the mixture diluted with 4 parts of water, boiled, cooled, diluted to 1 litre, filtered, and an aliquot portion of the filtrate acidified with acetic acid and titrated with uranyl acetate solution. W. P. S.

Estimation of Phosphoric Acid. I. (1) The Estimation of Phosphoric Acid as Magnesium Ammonium Phosphate and the Hindrance of its Precipitation by the Serum Constituents. (2) The Estimation of Phosphoric Acid as Uranium Phosphate and as Silver Phosphate. HANS KLEINMANN (*Biochem. Zeitsch.*, 1919, **99**, 19—45).—Serum constituents, such as potassium dihydrogen phosphate, urea, glycine, or calcium carbonate, do not influence the precipitation of phosphoric acid as magnesium ammonium phosphate. The presence of sodium chloride in certain concentrations, on the other hand, leads to high results. Reagents, such as picric acid and trichloroacetic acid, employed in the precipitation of proteins influence the precipitation, although they do not hinder it. Serum does not contain any substances which are capable of preventing the complete precipitation of phosphoric acid as magnesium ammonium phosphate. On precipitating 1 mg. of P_2O_5 as magnesium ammonium phosphate in 50—75 c.c. of solution, 0·006 mg. remains unprecipitated. With a smaller quantity (0·1 mg.) of P_2O_5 the unprecipitated fraction is even proportionately higher. The uranium acetate method yields good results with quantities as low as 10 mg. of P_2O_5. Quantities below 10 mg. give untrustworthy results. With Liebermann's silver phosphate method high results are obtained, whilst the estimation of phosphoric acid as the vanadium–phosphoric acid–molybdenum complex is found satisfactory. Columbium and tantalum produce no specific coloration with phosphoric acid and molybdenum. S. S. Z.

Estimation of Phosphoric Acid. II. The Estimation of Phosphoric Acid in Phosphomolybdates. Gravimetric and Colorimetric Methods. HANS KLEINMANN (*Biochem. Zeitsch.*, 1919, **99**, 45—95).—The precipitation of molybdenum by Raper's method gives too high values. Preliminary colorimetric experiments have shown that the coloured compounds produced by molybdenum with tannin or the phenols are entirely unsuitable for quantitative analysis. The phenylhydrazine compounds yield untrustworthy results, but the molybdenum-red reaction (potassium thiocyanate) is satisfactory. The most suitable results are obtained with potass-

ium ferrocyanide. One mg. of molybdenum was estimated in 100 c.c. with an error of 0·5%. The procedure was successfully applied for the colorimetric estimation of phosphoric acid, which was precipitated as phosphomolybdate and the molybdenum then estimated colorimetrically with potassium ferrocyanide; 0·1 mg. of P_2O_5 can be estimated by this method with an error of 0·5%. An attempt to devise a satisfactory method for the estimation of ammonium in the phosphoric acid molybdenum complex failed. S. S. Z.

Estimation of Phosphoric Acid. III. The Estimation of Phosphoric Acid in Phosphomolybdates. Volumetric and Sedimetric Methods. HANS KLEINMANN (*Biochem. Zeitsch.*, 1919, **99**, 95—115).—Low results were obtained with Neumann's method for the estimation of phosphorus when the theoretical factor was used. By washing the ammonium phosphomolybdate precipitate with 50% alcohol instead of water, better results were obtained. In micro-Neumann estimations it is more satisfactory to wash the precipitate than to centrifuge it, as a certain amount of loss is thus obviated. The author describes a "sedimetric" method by means of which the phosphorus is rapidly estimated by measuring the volume of the precipitate after centrifuging it in a graduated tube. The height of the ammonium phosphomolybdate precipitate is proportional to its P_2O_5-content. S. S. Z.

Estimation of Phosphoric Acid. IV. The Estimation of Phosphoric Acid as a Strychnine-Phosphoric Acid-Molybdenum Compound (Nephelometry). The General Principles of Nephelometry and the Construction of a New Nephelometer. HANS KLEINMANN (*Biochem. Zeitsch.*, 1919, **99**, 115—150).—A description of the development of nephelometry. A new nephelometer and its manipulation are also described.

S. S. Z.

Estimation of Phosphoric Acid. V. The Estimation of Phosphoric Acid as a Strychnine-Phosphoric Acid-Molybdenum Compound. Special Phosphoric Acid Nephelometry and a New Method of Preparation of the Strychnine-Molybdenum Reagent. HANS KLEINMANN (*Biochem. Zeitsch.*, 1919, **99**, 150—190).—Strychnine sulphate and sodium molybdate react in moderately concentrated hydrochloric acid solution to form a clear, colourless, stable reagent, which is suitable for the estimation of phosphoric acid; 0·1—0·0005 mg. of P_2O_5 can be estimated in this way by a nephelometric method with an error of 0·5%. S. S. Z.

Estimation of Minute Quantities of Arsenic by Titration. H. H. GREEN (*J. S. African Assoc. Anal. Chem.*, 1920, **3**, 3—4).—For quantities of arsenic trioxide ranging from 0·05 to 5 mg., the solution containing the arsenic is treated as usual in a Marsh apparatus and the evolved gases are passed successively through a vessel

containing lead acetate solution and three vessels containing dilute silver nitrate solution. The contents of the silver nitrate vessels are then mixed, treated with sodium hydrogen carbonate, solid potassium iodide is added until the precipitated silver iodide has re-dissolved, and the mixture is titrated with $N/500$-iodine solution. Each c.c. of the latter is practically equivalent to 0·1 mg. of arsenic trioxide. The black silver precipitate need not be removed before the titration is made. W. P. S.

Electrometric Analysis of Arsenicals. CHARLES S. ROBINSON and O. B. WINTER (*J. Ind. Eng. Chem.*, 1920, **12**, 775—778).—The electrometric apparatus used is essentially that described by Hillebrand (A., 1913, ii, 721), except that a mechanical stirrer is added and a reflecting galvanometer of the box type employed in place of the capillary electrometer. The titration of arsenic trioxide is made with iodine solution in the presence of sodium hydrogen carbonate, whilst arsenic pentoxide is titrated at 95° in 50% sulphuric acid solution with sodium iodide solution. The method is particularly suitable for the estimation of arsenic in coloured solutions.
W. P. S.

Estimation of Carbon Dioxide in Carbonates Insoluble in Water. C. S. ROBINSON (*Soil Sci.*, 1920, **10**, 41—47).—Estimations were made of the carbonate content of samples of limestone, marl, and soil. The first method used was that of Van Slyke (A., 1919, ii, 78). The second method was a gasometric one, originally proposed for soluble carbonates by Van Slyke (A., 1917, ii, 422). A special form of cup nitrometer was used, with a tube and special stopper holding the weighed sample introduced between the end of the nitrometer and the levelling tube, which contained mercury. The apparatus having been freed from air, hydrochloric acid was introduced from the cup. After all the gas was evolved, its volume was measured and its weight calculated from tables prepared for the conditions of the determination. The gasometric method was the more accurate of the two, but the first method was to be preferred for samples low in magnesium carbonate. J. H. J.

Micro-method for the Estimation of the Carbon Dioxide of the Blood. A. KROGH and G. LILJESTRAND (*Biochem. Zeitsch.*, 1920, **104**, 300—315).—Various modifications are introduced into Barcroft and Haldane's method for estimating the carbon dioxide of the blood (A., 1902, ii, 424); 0·25—0·3 c.c. of blood suffices for two estimations, the mean error of the result being ±0·5% by volume. T. H. P.

Estimation of Potassium and Sodium Present Together. A. QUARTAROLI (*Gazzetta*, 1920, **50**, ii, 64—69).—The disadvantages of the ordinary methods for estimating separately potassium and sodium may be overcome by converting the weighed mixture of the chlorides into nitrates and determining the melting

point of the mixed nitrates, first alone, and, secondly, after admixture with an equal weight of pure potassium nitrate; the melting-point curve falls sharply from 336° (KNO_3) to 220° (about 55% KNO_3), and then rises sharply to 306° ($NaNO_3$). If P represents the weight of the mixed chlorides and a the percentage of potassium nitrate in the mixed nitrates, as indicated by the melting point, then the weight of potassium chloride in the weight P of mixed chlorides will be given by $x = 1·0723aP/(0·0723a + 100)$. [See also *J. Soc. Chem. Ind.*, 1920, October.] T. H. P.

Estimation of Total Calcium in Soils and the Significance of this Element in Soil Fertility. O. M. SHEDD (*Soil Sci.*, 1920, **10**, 1—14).—A more rapid and accurate method than that already in use for the estimation of calcium in soils, and one in which the production of an ammonia precipitate, which occludes calcium, is avoided, is described. One gram of the sample is fused with fusion mixture and the silica separated in the usual manner. The filtrate is made just alkaline with ammonia, and then just acid with hydrochloric acid, heated to the b. p., and precipitated with 1—2 grams of solid ammonium oxalate. The mixture is kept on the steam-oven for a few hours, and then at the ordinary temperature overnight. The precipitate is filtered and ignited. The oxide or carbonate is dissolved in hot dilute hydrochloric acid, and bromine water and ammonia added to precipitate manganese. The solution is acidified with acetic acid, and the manganese filtered off. The filtrate is then reprecipitated as before.

Analyses by this method of a large number of soils, both cultivated and uncultivated, showed that cultivation led to a considerable loss of calcium. The more fertile soils contained the most calcium. The application to soils poor in calcium of limestone or rock phosphate is beneficial, on account of the calcium they supply as plant food, apart from any other benefit they confer.

J. H. J.

Estimation of Calcium in Small Quantities of Blood Serum. BENJAMIN KRAMER and JOHN HOWLAND (*J. Biol. Chem.*, 1920, **43**, 35—42).—One or 2 c.c. of serum are evaporated to dryness in a platinum crucible and gently incinerated. The ash is dissolved in a small quantity of N-hydrochloric acid, and the solution again evaporated to dryness and incinerated. The crystalline residue is readily soluble in not more than 1 c.c. of $0·1N$-sulphuric acid, and this solution is quantitatively transferred to a special type of 2 c.c. calibrated tube. After neutralisation by ammonia and warming, the calcium is precipitated by an excess (0·3 c.c.) of $0·1N$-oxalic acid in $0·05N$-sulphuric acid. The reaction must be acid at this point. Heating is continued for a few minutes, 0·1 c.c. of a saturated solution of sodium acetate is added, the tube is well shaken, and the volume is made up to 2·0 c.c. After several hours, the precipitate is filtered through a hardened filter, and the excess of oxalic acid in 1 c.c. of the filtrate is estimated by titration with $0·01N$-potassium permanganate. A

blank estimation on the reagents is necessary. The method appears to be trustworthy.

The results previously reported by Howland and Marriott (A., 1918, ii, 21) on the calcium of the serum in infantile tetany are confirmed. J. C. D.

Use of Organic Solvents in the Quantitative Separation of Metals. III. Separation of Magnesium from Sodium and Potassium Chlorides. S. Palkin (*J. Amer. Chem. Soc.*, 1920, **42**, 1618—1621. Compare A., 1917, ii, 43).—The method previously published for the separation of lithium from sodium and potassium (*loc. cit.*) has been modified and adapted to the separation of magnesium from sodium and potassium. The modified method depends on a progressive precipitation of the sodium and potassium chlorides from a concentrated solution by the use of alcohol and ether, and is divided into two stages: (i) in which all but a few milligrams is precipitated, and (ii) in which the last few milligrams are removed from solution. The estimation is carried out as follows: the total chlorides of magnesium, sodium, and potassium are dissolved in the minimum quantity of water (about 1·5 c.c. of water are sufficient for 0·5 gram of substance), one drop of concentrated hydrochloric acid is added, and gradually 25 c.c. of absolute alcohol are dropped into the liquid while rotating. The sodium and potassium chlorides should precipitate in a uniform granular condition. In a similar manner, 25 c.c. of ether are added, and the mixture is kept until the precipitate is agglomerated and the supernatant liquid nearly clear. The mixture is filtered, and the beaker and precipitate are washed with a mixture of one part of alcohol and four parts of ether. The filtrate is evaporated to dryness on a steam-bath; the residue is dissolved in 10 c.c. of alcohol, one drop of concentrated hydrochloric acid added, and the mixture warmed until practically everything has dissolved. The beaker is then rotated and 50 c.c. of ether slowly added, and the mixture kept for twenty minutes. The precipitate is collected on the same filter, washed with the ether-alcohol mixture, dried, ignited, and weighed. The filtrate containing the magnesium is evaporated nearly to dryness, dissolved in 5—10 c.c. of concentrated hydrochloric acid and a little water, sodium hydrogen phosphate is added, and the estimation completed in the usual way. The method has several advantages over the usual method, namely, (i) it affords a direct estimation of the sodium and potassium salts, inasmuch as they are precipitated first rather than after the magnesium, (ii) the reagents used are volatile organic solvents, and (iii) no foreign salt or base is introduced as a precipitating agent. J. F. S.

Magnesia Mixture. O. Kuhnt (*Chem. Zeit.*, 1920, **20**, 586).—If "magnesia mixture" is prepared without the addition of ammonia, it may be kept for an indefinite period in glass bottles without the glass being attacked, with the consequent formation of a precipitate in the reagent. The absence of ammonia does not

interfere with the use of the reagent for the precipitation of pho phoric acid; only a slight excess of the reagent should be employe and ammonia added subsequently in sufficient quantity.

W. P. S.

Estimation of Small Amounts of Copper by the Iodid Method. H. F. Bradley (*J. Ind. Eng. Chem.*, 1920, **12**, 800).- The precipitate of cupric sulphide is washed, moistened with few drops of concentrated zinc nitrate solution, and ignited. Th residue of oxides is dissolved in dilute hydrochloric acid (1:1), th solution neutralised with 5% potassium hydroxide solution, acidifie with acetic acid, a small amount of phosphate solution is adde followed by 2 grams of sodium iodide, and the liberated iodine titrated.

W. P. S.

Estimation of Mercury in Urine. R. Fabre (*J. Pharn Chim.*, 1920, [vii], **22**, 81—85).—One litre of the urine is heate under a reflux apparatus with 100 c.c. of hydrochloric acid, an 6 grams of potassium chlorate are added in small quantities at time during a period of about two hours. The solution is boile under the reflux apparatus to expel the greater part of the fre chlorine, cooled, treated with sulphur dioxide, and again boile After filtration, the solution is treated with 15 c.c. of stannou chloride solution, heated for two hours on a water-bath, and a the end of twenty-four hours the liquid is decanted from the gre precipitate. The latter is treated with a few c.c. of hydrochlori acid to cause the mercury to collect in a globule, which is washe with water, alcohol, and ether, dried over sulphuric acid, an weighed. If the quantity of mercury is very small, it may b collected on a gold-coated asbestos filter, as recommended b Farup.

W. P. S.

Some Microchemical Methods. Alfred Brammall (*Geo Mag.*, 1920, **57**, 123—125).—The following microchemical tests fo iron and manganese are described. (1) *Detection of iron:* The cove glass is removed, and the slide is cleansed of balsam, polished, agai cleansed, and warmed. Reaction paper is prepared by soaking piece of white drawing paper in concentrated hydrochloric acid and pres ing them in similar sheets until no longer wet. An ammonium thio cyanate paper is similarly prepared. The acid paper is carefully lai on the section, covered with a strip of cardboard on which is laid hot iron for two or three minutes. After the slide has dried, th thiocyanate paper is similarly applied, pressed in the cold, and agai dried. The distribution of ferric iron is revealed by a transparen blood-red stain of ferric thiocyanate. Potassium ferrocyanide sim larly used gives an opaque blue coloration which must be examine in reflected light. The method was found valuable in the examina tion of the "spotted rocks" of Andlauthal, Vosges; of dark incl sions in, and alterations of chiastolite; lamination in shales; ident fication of magnetite, siderite, etc. (2) *The fusion test for man ganese* may be applied to slides as follows: A slide is ground dow

and one side polished. The slide is then detached from the glass slip, and cleansed from balsam and dried. It is allowed to soak for several minutes in a hot saturated solution of potassium carbonate and nitrate and dried. A thin wash of the solution is applied to the polished surface and allowed to dry. This surface is subjected to the f. p. tip of the blowpipe flame for a few minutes, and after cooling is slightly polished to level the veneer of the fusion. After remounting on the slide with the prepared surface downward, the section is ground thin and examined by transmitted light. (3) *Obscure bedding planes and minute structures in chalk and limestone* may be revealed by differential solution of ground and polished sections in a bath of carbonated waters, a method approximating to weathering. CHEMICAL ABSTRACTS.

The Adsorption of Copper Oxide and Nickel Oxide by Precipitates of Ferric Oxide. ER. TOPORESCU (*Compt. rend.*, 1920, **171**, 303—305).—By the addition of ammonium hydroxide to a solution of a ferric salt containing in addition either a copper salt or a nickel salt a certain amount of copper oxide or nickel oxide is always adsorbed by the ferric hydroxide, the amount depending on the relative proportions of the two salts present and the amount of ammonium hydroxide added. These oxides cannot be removed from the ferric oxide by washing the precipitate or by treatment with concentrated ammonia solution. W. G.

Analysis of Zirconium Minerals. H. V. THOMPSON (*Pottery Gaz.*, 1920, **45**, 767).—In the analysis of zirconium ores two main difficulties are encountered: (1) raw zirconium ores and products manufactured therefrom are not easily decomposed, and (2) the separation of aluminium from zirconium is not readily effected. Use is made of the fact that after fusion with sodium peroxide and decomposition of the fusion with water, the residue contains all the iron, titanium, and zirconium in the form of oxides together with some of the silica, whilst the whole of the aluminium and the remainder of the silica are contained in the filtrate. This process possesses the advantage that zirconium and aluminium are automatically separated during the decomposition of the sample.
CHEMICAL ABSTRACTS.

Differential Analysis of Acetone, Acetaldehyde, and Formaldehyde in Organic Liquids. EMILIO PITTARELLI (*Arch. farm. Sper. sci. Aff.*, 1920, **29**, 70—87).—The various methods, depending on precipitation, coloration, or odour, for the detection of acetone, acetaldehyde, and formaldehyde are described and discussed as regards their application to fermented liquids, milk, urine, etc. In the examination of urine, the free acetone may be separated by treatment with excess of Nessler's reagent, and the combined acetone by distilling the filtrate with an acid. T. H. P.

Colour Reaction of Milk in Presence of Formaldehyde. ARTURO ROSSI (*Boll. Chim. Farm.*, 1920, **59**, 265—268).—The pres-

ence of formaldehyde in milk may be detected by adding 2—2·5 c.c. of the milk carefully to 2 c.c. of sulphuric acid (D 1·820—1·825) in a test-tube, so that the liquids mix as little as possible, and then shaking the tube rapidly; the liquid assumes a more or less intense violet colour, according to the proportion of formaldehyde present. The best conditions for the reaction vary with such proportion, the sensitiveness diminishing with more than 0·0005% of the aldehyde; in doubtful cases the samples to be tested may be diluted with pure milk. Other substances may be examined for formaldehyde by subjecting them to distillation, mixing part of the distillate with pure milk, and applying the sulphuric acid reaction. Milk free from formaldehyde sometimes gives this violet coloration, but only after being in contact with the sulphuric acid for some hours. T. H. P.

Estimation of Minute Amounts of Acetone by Titration. ROGER S. HUBBARD (*J. Biol. Chem.*, 1920, **43**, 43—56).—A modification of the Messinger titration method suitable for dilute solutions of acetone. The conditions necessary for an accurate estimation have been carefully worked out and are fully described.

A method of successive distillation from acid, alkaline, and oxidising solutions is described, whereby acetone may be separated from much larger amounts of alcohol and other interfering substances. J. C. D.

Estimation of Acetone in Expired Air. ROGER S. HUBBARD (*J. Biol. Chem.*, 1920, **43**, 57—65).—The patient breathed for five precipten minutes through a mask or through a mouthpiece, the acid to d air passing through two bottles containing 75 c.c. of a with watprepared 2·5% solution of sodium hydrogen sulphite. For weighed. val of interfering substances the contents of the bottles collected oilled successively with 10% sodium hydroxide solution Farup. tassium permanganate solution, and a solution of sodium the final distillate, acetone is estimated either by the
Some Microcnabove (preceding abstract) or by the turbidity *Mag.*, 1920, **57**, 123—ott-Wilson reagent. J. C. D.
iron and manganese are t
glass is removed, and the **Micro-reduction.** D. G. COHEN TERVAERT
cleansed, and warmed. Reac1920, **110**, 41—54).—The experiments
of white drawing paper in cong's modified method for the micro-esti
ing them in similar sheets unti 1918, ii, 278, 279; this vol., ii, 199
cyanate paper is similarly prepan, i, 613; 1919, ii, 434) is applicable
on the section, covered with a stor a definite time.
hot iron for two or three minutemethod, consisting in oxidation by
thiocyanate paper is similarly applows of the estimation of dextrose
dried. The distribution of ferric i by this method, the reduction of
blood-red stain of ferric thiocyanatcated by the ordinary copper
larly used gives an opaque blue cold is estimated quantitatively by
in reflected light. The method was T. H. P.
tion of the "spotted rocks" of Anrose by Bang's Method
sions in, and alterations of chiastol*l. Chem.*, 1920, **109**, 57—64).—
fication of magnetite, siderite, etc (this vol., ii, 199) with quantities
... may be applied to slides as

of pure dextrose varying from 0·545 mg. to 0·027 mg., the ratio between the weight of dextrose (mg.) and the number of c.c. of 0·01*N*-iodate solution increasing from 1:2·78 to 1:1·19, whereas Bang and Hatlehoel (A., 1918, ii, 279) gave the constant value 1:2·8 for this ratio. No greater constancy of this ratio is achieved by the use of steam for boiling the solution. Hence, for the estimation of dextrose in the blood an empirical table is necessary. It is questionable if Bang's method really suffices for the estimation of sugar in a few drops of blood, and for the estimation of 1 mg. or less of dextrose, Bertrand's method is recommended. T. H. P.

Estimation of Minimal Quantities of Dextrose, specially in Blood. H. C. Hagedorn and B. Norman Jensen (*Ugeskrift for Laeger*, 1918, **80**, 1217—1228).—The method, which gives concordant results, depends on the precipitation of proteins by zinc hydroxide, the reduction of potassium ferricyanide by dextrose, and the iodometric estimation of the excess of ferricyanide. Blood, 0·1 c.c., is added to a mixture of 5 c.c. of 0·45% hydrated zinc sulphate solution and 1 c.c. of *N*/10-sodium hydroxide, the mixture is heated in a boiling water-bath for four minutes, cooled, and filtered; the tube, precipitate, and filter are washed thrice with 3 c.c. of water. Two c.c. of a solution (1·649 grams of potassium ferricyanide and 28·6 grams of sodium carbonate decahydrate in one litre, which will keep in the dark for at least two months) are added and the mixture is heated in a boiling water-bath for fifteen minutes. After cooling, 3 c.c. of a solution (5 grams of potassium iodide, 10 grams of hydrated zinc sulphate, and 50 grams of sodium chloride in 200 c.c.) and 2 c.c of 3% acetic acid are added, and the mixture is titrated with thiosulphate (1·24 grams of hydrated sodium thiosulphate in one litre, which must be standardised against potassium ferricyanide or 0·005*N*-potassium iodate). The difference between 2 c.c. and the volume of thiosulphate used is the volume of ferricyanide reduced by dextrose, the amount of which is determined by the following figures, in which the volume of ferricyanide in c.c. is followed by the amount of dextrose in mg.: 0·10, 0·017; 0·20, 0·035; 0·30, 0·053; 0·40, 0·070; 0·50, 0·088; 0·60, 0·106; 0·70, 0·124; 0·80, 0·141; 0·90, 0·159; 1·00, 0·177; 1·10, 0·195; 1·20, 0·214; 1·30, 0·232; 1·40, 0·251; 1·50, 0·270; 1·60, 0·290; 1·70, 0·310; 1·80, 0·331; 1·90, 0·355; 2·00, 0·384.

Chemical Abstracts.

Improved Method for the Detection of Sugar, particularly in Urine. Walter S. Haines, Gilbert P. Pond, and Ralph W. Webster (*J. Amer. Med. Assoc.*, **74**, 301—302; from *Chem. Zentr.*, 1920, iv, 240—241).—A modified Haines solution is recommended, for which copper sulphate (5 grams), glycerol (250 c.c.), potassium hydroxide (20 grams), or sodium hydroxide (14·3 grams) are dissolved in 1 litre with distilled water. The copper sulphate is dissolved in a warm mixture of water (250 c.c.) and glycerol (250 c.c.); the alkali is dissolved separately in water

(200 c.c.), after which the solutions are mixed and made up t(1000 c.c. Five c.c. of the solution are heated to boiling and treatec in an inclined test-tube with 10—20 drops of urine, the phosphat(of which has been precipitated and filtered after addition of 5—(drops of sodium hydroxide solution (5—10%). A red or yellow rin(is immediately formed at the junction of the solution and urine i the latter contains more than 0·1% of sugar; if only 0·03% i present, the ring only appears after a few seconds, but, at any rate within a minute. Smaller amounts of sugar, which then lie withi physiological limits, cannot be detected, so that a positive result o the test indicates a pathological condition. H. W.

Iodometric Estimation of the Phenyl Derivatives o Arsenious Acid. PAUL FLEURY (*Bull. Soc. chim.*, 1920, [iv], 27 699—704).—In continuation of previous work (this vol., i, 578) method has been devised for estimating arsenic trichloride, pheny dichloroarsine, diphenylchloroarsine, and triphenylarsine in mixture of the four compounds.

A benzene solution of the mixture is extracted with aqueou sodium hydroxide, whereby arsenious acid and phenylarseniou acid are extracted. This extract is acidified with hydrochloric ac until its acidity is approximately $N/10$, alcohol is added in equ volume, and the mixture is titrated with standard iodine solutio The iodine used is equivalent to the phenyldichloroarsine prese in the original mixture. An excess of sodium hydrogen carbonate added, and the titration is again completed. The further amount (iodine required is equivalent to the arsenic trichloride original present. The benzene solution left after the extraction with alka is titrated with standard iodine solution, the amount required bei equivalent to the diphenylchloroarsine and triphenylarsine origi ally present. To the product from this titration an excess of aqueo sodium hydrogen carbonate is added, and the whole is extract with chloroform. The chloroform extract contains triphenylarsi oxide, and if the aqueous solution is now acidified and aga extracted with chloroform, the second extract will contain dipheny arsenic acid, which may be obtained in a crystalline form (evaporation of the solvent. W. G.

Estimation of Volatile Acids in Fermentation Product G. HINARD (*Ann. Chim. Analyt.*, 1920, [ii], **2**, 239—242).—Fif c.c. of the liquid are mixed with 10 c.c. of water and distilled, 50 c. of distillate being collected and titrated. Fifty c.c. of water are th added to the contents of the distillation flask, and a second quanti of 50 c.c. is distilled and titrated. These operations are repeat several times and a curve plotted from the results; the asympto of this curve indicates the amount of alkali solution required neutralise the total volatile acids present. W. P. S.

Isolation of Formic, Acetic, and Lactic Acids. ISSNOSU ONODERA (*Ber. Ohara Inst. landw. Forsch.*, 1917, i, 231—259; fro *Chem. Zentr.*, 1920, iv, 271).—The three acids are extracted fro

the mixed solution by means of ether. In one portion of the ethereal solution formic acid is titrated with permanganate, and, in this oxidised portion, the lactic acid is estimated as oxalic acid. Acetic acid is removed from the decomposed solution by means of ether, and the extract is again distilled. The method is trustworthy, and its accuracy is not influenced by the presence of small amounts of propionic and butyric acids. H. W.

The Colorimetric Estimation of Tyrosine by the Method of Folin and Denis. ROSS AIKEN GORTNER and GEORGE E. HOLM (*J. Amer. Chem. Soc.*, 1920, **42**, 1678—1692).—Tyrosine cannot be estimated quantitatively in the products of protein hydrolysis by means of the phenol reagent of Folin and Denis (A., 1912, ii, 1012). Tryptophan, if present, will give an intense colour with the reagent, and indole and indole derivatives, as well as ferrous salts, also give the blue colour. It seems probable that other products of protein hydrolysis may also produce blue colours with the phenol reagent. Further, in the case of tyrosine itself the depth of colour varies with the relative proportion of reagent and tyrosine present, the colour values falling off sharply as the concentration of the tyrosine increases. Protein hydrolysates must not be decolorised with carbon or bone charcoal if they are to be used subsequently for the estimation of amino-acid content, as tyrosine, tryptophan, and its decomposition products are adsorbed in appreciable amounts by bone-black. Bone-black itself contains some easily oxidisable material, which dissolves in acid solutions and then gives the blue colour with the phenol reagent. W. G.

Estimation of Uric Acid by Clarification of the Liquids by means of Talc. E. LAMBLING and C. VALLÉE (*Compt. rend. Soc. Biol.*, 1920, **83**, 793—795; from *Chem. Zentr.*, 1920, iv, 217). —A portion of the uric acid is carried down by talc even from acid solutions. H. W.

Analytical Characters of Dichlorodiethyl Sulphide. FELIX MARTIN (*J. Pharm. Chim.*, 1920, [vii], **22**, 161—165).—$\beta\beta'$-Dichlorodiethyl sulphide ("mustard gas"), after oxidation, gives the usual reaction for sulphuric acid. When a small quantity of the substance is heated with alcoholic potassium hydroxide solution, and the vapours produced are passed into Denigès's reagent (an acid solution of mercuric sulphate), a white precipitate is formed; if the vapours are absorbed in water, the solution, on treatment with a drop of iodine solution, yields an odour similar to that of mercaptan. Dichlorodiethyl sulphide is hydrolysed by water, and the solution yields a turbidity when treated with Grignard and Rivat's reagent (iodine 8 grams, gum arabic solution 1 c.c., copper sulphate 0·8 gram, and water 33 c.c.). W. P. S.

Behaviour of Phenolphthalein with Iodine and a Method for the Estimation of Phenolphthalein. SAMUEL PALKIN (*J. Ind. Eng. Chem.*, 1920, **12**, 766—769).—Investigation of the

action of iodine on phenolphthalein relative to the conditio governing the formation of tetraiodophenolphthalein and t physical properties of the latter, yielded information on which w based the following method for the estimation of the substanc The phenolphthalein is dissolved in 30% potassium hydroxide sol tion and a small quantity of water, 20 grams of ice are added, an then an excess of iodine reagent (10% of iodine in 15% potassiu iodide solution, the free iodine being then combined by the add tion of alkali). Concentrated hydrochloric acid is now added unt precipitation is complete, more iodine is added if the liquid is n brown in colour, the precipitate is dissolved by the addition 30% potassium hydroxide solution, and the precipitation and sol tion repeated three or four times. The final alkaline solution treated with 0·5 c.c. of 10% sodium sulphite solution, acidified wi hydrochloric acid, and extracted several times with aceton chloroform mixture (1 : 3); the united extracts are evaporated, t residue of tetraiodophenolphthalein dried at 100°, and weighe The weight multiplied by 0·3781 gives the amount of pheno phthalein present. W. P. S.

Estimation of Codeine. H. E. Annett and Haridas S (*Analyst*, 1920, **45**, 321—328).—The following method may applied to opium, pure alkaloids, plant materials, etc., with su able modification of the amounts of substance taken. Ten gra of dry opium are mixed thoroughly with 4 grams of calcium hyd oxide and 100 c.c. of water, the mixture stirred for thirty minut filtered, and 50 c.c. of the filtrate are treated with 40 c.c. of acetic acid and 10 c.c. of basic lead acetate solution (D 1·2 After filtration, 75 c.c. of the filtrate are shaken with 2 grams calcium hydroxide for thirty minutes, the mixture filtered, a 50 c.c. of the filtrate are extracted with three successive quantit of 50 c.c. of toluene. The combined toluene extract is filte and treated with dry hydrogen chloride, avoiding any great exc of the latter. Codeine hydrochloride separates, and, after exc of hydrogen chloride has been expelled by a current of air, collected, dissolved in water, the solution evaporated, and t residue of codeine hydrochloride dried and weighed. W. P. S.

Colour Tests for Nitrates and Nitrites, Antipyrine (Pyramidone), Phenol and Aniline, and α- and β-Naphthol A. Escaïch (*J. Pharm. Chim.*, 1920, [vii], **22**, 138—141).—T author's colour test for nitrites (A., 1918, ii, 273) gives uncerta results with natural waters rich in chlorides, but the latter m first be removed by means of silver nitrate. When the nitrates the water are to be reduced to nitrites by amalgamated aluminiu this process must precede the precipitation of chlorides. Ma nesium, like aluminium, may be activated by immersion in mercu cyanide solution and used for reducing nitrates to nitrites. colour test is described for the detection of antipyrine pyramidone, based on the production of violet and red coloratio by conversion of antipyrine into nitrosoantipyrine, and oxidati

of the latter with lead peroxide. A very sensitive test for phenol in aqueous solutions is to treat 10—15 c.c. with five to ten drops of ammonia, 0·05—0·1 gram of sodium persulphate, and four or five drops of $N/10$-silver nitrate solution. A green coloration is produced, which changes to blue or yellow, according as the concentration of phenol was more or less than about 0·05 gram per litre. α-Naphthol dissolved in aqueous alcohol and treated with sodium nitrite and a few drops of acid mercuric sulphate solution gives a fine, red coloration and red precipitate, whilst β-naphthol gives a yellow precipitate. J. H. L.

Estimation of Phenol in the Presence of certain other Phenols. ROBERT M. CHAPIN (*J. Ind. Eng. Chem.*, 1920, **12**, 771—775).—The method depends on the red coloration yielded by phenol with Millon's reagent when the mixture is heated in the presence of nitric acid; most other phenols give yellow colorations, but β-naphthol gives a brown, and salicylic acid a red, colour. It is necessary to heat the mixture at 100° for thirty minutes in order to discharge the original red colour given by the other phenols and to allow the red colour of phenol itself to reach its full intensity. Various modifications of the method are described which are suitable for different requirements. The red coloration given by phenol may be reduced to yellow by the action of formaldehyde, whilst any yellow colour present originally is not affected. [See, further, *J. Soc. Chem. Ind.*, 1920, 652A.] W. P. S.

Method for the Estimation of Cineole in Eucalyptus Oils. T. TUSTING COCKING (*Pharm. J.*, 1920, **105**, 81—83).—Three grams of the eucalyptus oil, dried previously over calcium chloride, are mixed with 2·1 grams of *o*-cresol, and the solidifying point of the mixture is determined. The quantity of cineole present is ascertained by reference to a graph. W. P. S.

Estimation of Urea in Blood in Normal and Pathological Cases; Comparative Results of the Hypobromite and Xanthhydrol Methods. M. LAUDAT (*Compt. rend. Soc. Biol.*, 1920, **83**, 730—732; from *Chem. Zentr.*, 1920, iv, 68).—Considerable errors are involved in the estimation of urea in blood by the hypobromite method, since ammonia, uric acid, and creatine are decomposed by the reagent to a greater or less extent. Xanthhydrol, on the other hand, does not attack these substances. H. W.

Estimation of Urea in Blood by Xanthhydrol. W. MESTREZAT and MARTHE JANET (*Compt. rend. Soc. Biol.*, 1920, **83**, 763—764; from *Chem. Zentr.*, 1920, iv, 217).—The experimental conditions necessary for an exact estimation have been investigated.

The xanthhydrol method is no longer exact in a 1% solution of urea; Tanret's reagent dissolves xanthylurea. The serum (10 c.c.) is diluted to such an extent that it contains about 0·5 gram of

urea per litre, treated with concentrated Tanret's reagent (10 c.c.) and centrifuged. The clear liquid is treated under definite con ditions with pure acetic acid and a 10% solution of xanthhydro in absolute methyl alcohol; after three hours, the xanthylcarbamid is filtered through a Gooch crucible, washed with absolute methy alcohol, dried at 70°, and weighed. H. W.

Estimation of Urea by Xanthhydrol. FRENKEL (*Ann Chim. Anal.*, 1920, [ii], **2**, 234—239).—Ten c.c. of a 10% solu tion of urine are treated with 35 c.c. of glacial acetic acid, an 1 c.c. portions of 10% xanthhydrol solution (in methyl alcohol) ar added at intervals of ten minutes until 5 c.c. have been introduced After one hour, the precipitate formed is collected, washed wit alcohol, dried at 100°, and weighed; the weight is divided by to obtain the amount of urea. Other substances found in urin do not give a precipitate with the reagent. The method may b applied to the estimation of urea in blood after this has bee treated with mercuric chloride–potassium iodide reagent (mercuri chloride 2·71 grams, potassium iodide 7·20 grams, glacial aceti acid 66 c.c., and water 100 c.c.), and filtered. W. P. S.

Micro-method for the Estimation of Urea in Blood an Organic Secretions. K. L. GAD-ANDRESEN (*Biochem. Zeitsch* 1919, **99**, 1—19).—The proteins are precipitated with 0·01*N*-aceti acid in the presence of sodium acetate, and the urea is estimate in the filtrate with sodium hypobromite. The nitrogen evolve is measured with Krogh's microrespirometer, and the result calcu lated by means of Krogh's formula. A correction is made for th nitrogen evolved by other substances. Only 0·1 c.c. or 0·15 c.c of blood is required. The occasional error is of the magnitude o 0·5 mg. per 100 c.c. Comparisons with the urease method showe good agreement. This method is applicable to blood and variou secretions of the organism. It is not suitable for the estimatio of urea in muscle tissue. S. S. Z.

Estimation of Hydrocyanic Acid. R. LEITCH MORRI (*Pharm. J.*, 1920, **105**, 83—85).—Liebig's method (titration wit silver nitrate solution) is trustworthy for the estimation of hydro cyanic acid provided that the acid is neutralised previously; an great excess of alkali must be avoided, and this is best attaine by using borax solution in place of sodium hydroxide for th neutralisation (Guerin's modification). Excess of borax does no interfere. Volhard's method is useful in special cases, but entail the separation of the silver cyanide by filtration before the exces of silver nitrate can be titrated. Mohr's method (titration wit silver nitrate after neutralisation with magnesium oxide, an using potassium chromate as indicator), and Denigès' modificatio of Liebig's method (titration in alkaline solution, using potassiu iodide as indicator), are also trustworthy, but in the latter it i essential to use a sufficient quantity of potassium iodide. Ford and Gelis' iodometric method is suitable for the estimation o cyanide in mercury cyanide. W. P. S.

Hydrocyanic Acid in Phaseolus lunatus. J. A. SIMPSON (*Anal. Acad. Cien. Med. Fis. Nat. Habana*, 1918—1919, **55**, 250—283; *Expt. Sta. Rec.* **42**, 7).—To estimate hydrogen cyanide, he crushed beans were heated with dilute sulphuric acid, and the distillate was collected in sodium or potassium hydroxide solution. This was heated with calcium polysulphide and titrated with 5% erric sulphate until the colour of ferric thiocyanate developed. With care, the method is accurate to 0·00001 gram HCN. Of the varieties examined, "Rangoon blanca" gave 40 mg. HCN per 00 (grams?). Several gave between 3 and 8 mg. per 100 (grams?). The rest gave negative results. CHEMICAL ABSTRACTS.

Modification of the Van Slyke Method for Estimating Arginine. A. E. KOEHLER (*J. Biol. Chem.*, 1920, **42**, 267—268).—Van Slyke's method (compare A., 1916, ii, 62) is modified by drawing a slow current of air through the liquid during the digestion, he apparatus for absorbing the ammonia being a simple gas washbottle. W. G.

Volumetric Estimation of Diazo-compounds by Reduction. EDMUND KNECHT and LEONARD THOMPSON (*J. Soc. Dyers and Col.*, 1920, **36**, 215—219).—Benzenediazonium chloride in dilute ydrochloric acid solution may be titrated with titanous chloride olution, using H-acid as external indicator. The reaction requires wo equivalents of hydrogen, and takes place without simultaneous ormation of phenylazoimide and aniline. The titration may lso be carried out by adding an excess of titanium trichloride olution and titrating the excess with acid-green solution in the resence of sodium tartrate. Methods are also described for the tration of sodium *p*-nitro*iso*diazobenzene with titanium trichloride olution or sodium hyposulphite solution. [See, further, *J. Soc. Chem. Ind.*, 1920, 594A.] W. P. S.

Proteins and Some New Methods of Investigating their Composition. A. C. ANDERSEN (*K. Vet. Landbohöjskole Aarskrift*, 917, 308—334; from *Chem. Zentr.*, 1920, iv, 113).—Van Slyke's nethod of analysing proteins is modified by separating the fifth raction (amino-nitrogen) into two sub-fractions; the first of these ontains glycine, alanine, serine, phenylalanine, tyrosine, valine, nd the three isomeric leucines as monoamino-monocarboxylic acids, whilst the second comprises the monoamino-dicarboxylic compounds, spartic and glutamic acids. When an aqueous solution of a nixture of these amino-acids is neutralised with sodium hydroxide n the manner recommended by Sörensen for the formaldehyde tration, the monoamino-monocarboxylic acids, together with roline and oxyproline, remain uncombined, whilst the monoamino-carboxylic acids react with one equivalent of base. After vaporation of such a solution and incineration of the residue, odium carbonate is left in amount equivalent to the monoamino-carboxylic acids present. Exact directions for performing the nalyses are given. H. W.

The Estimation of Hæmatin in the Whole Blood. Fr Vlès (*Bull. Soc. chim. Biol.*, 1920, **2**, 125—132).—Two metho depending on the transformation of a mixture of oxyhæmoglob and hæmatin into one of reduced hæmoglobin and reduced alkali hæmatin, or one of carboxyhæmoglobin and reduced alkali hæmatin, respectively, are described. The estimation is carri out by spectrophotometric means. J. C. D.

A Method for the Estimation of Methæmoglobin a Hæmoglobin in Blood. W. S. McEllroy (*J. Biol. Chem.*, 19 **42**, 297—300).—The total hæmoglobin (methæmoglobin + hæ globin) is determined colorimetrically as hæmoglobin, us potassium ferricyanide to convert the hæmoglobin into methæ globin. The oxygen capacity is determined by Van Slyke's metl (compare A., 1918, ii, 82), from which is calculated the hæ globin. The difference between the two values is the amount methæmoglobin. W. G

A Quantitative Method for Estimation of Vitami Roger J. Williams (*J. Biol. Chem.*, 1920, **42**, 259—265. C pare A., 1919, i, 463).—It has been shown that the num of yeast cells produced from a single cell in eighteen hours un given conditions is a measure of the amount of vitamine pre (compare Bachmann, A., 1919, i, 613). The method is modified, and is gravimetric. A culture solution contair 20 grams of sucrose, 3·0 grams of ammonium sulphate, 2·0 gr latL potassium phosphate, 1·5 grams of asparagine, 0·25 gram nitrogam chloride, and 0·25 gram of magnesium sulphate in 1 l of blood : is prepared. To 100 c.c. of this solution a known amo 0·5 mg. pertion to be tested is added, and the mixture is made good agreemennd pasteurised or sterilised. To this is added 1 secretions of thede yeast suspension containing 0·3 gram of f of urea in muscle and the whole is incubated for eighteen hour

Estimation of maldehyde is added to stop growth, any gro
(*Pharm. J.*, 1920, 1C he surface is removed by a copper gauze sc
silver nitrate solution) n filtered off on a Gooch crucible, washed
cyanic acid provided th for two hours, and weighed. The weigh
great excess of alkali m minus the weight obtained in a contro
by using borax solution o the amount of vitamine added.
neutralisation (Guerin's m s a "vitamine number," this being
interfere. Volhard's metho yeast produced by 1 gram of the mat
the separation of the silver wn by experiment that nothing ex
of silver nitrate can be titra ounts used will materially improve
silver nitrate after neutralis contains asparagine in addition
using potassium chromate as i. W. (
of Liebig's method (titration i
iodide as indicator), are also t
essential to use a sufficient qua
and Gelis' iodometric method
cyanide in mercury cyanide.

General and Physical Chemistry.

Refractivities of Saturated and Unsaturated Compounds. GERVAIS LE BAS (*Trans. Faraday Soc.*, 1920, **15**, 231—237).—Further applications of the author's calculations to organic compounds (see A., 1918, ii, 49, 281). Negative anomalies are found with furfuraldehyde and thiophen. In pyridine there is an anomaly equal to that due to two and a-half ethenoid linkings. Other aromatic compounds, and substances containing the carbonyl group, are considered. J. R. P.

Size of the Alkali Cations and Halogen Anions. ADOLPH HEYDWEILLER (*Zeitsch. Physik*, 1920, **1**, 393—394).—Refraction data are used as a check on values obtained by Born and Landé from Born's crystal-grating theory. For the methods, previous papers are referred to. The agreement is considered excellent, and favourable to Born's theory. CHEMICAL ABSTRACTS.

A Simple Spectrometer for Laboratory Use. GÜNTER SCHEIBE (*Zeitsch. physiol. Chem.*, 1920, **110**, 229—232).—A description of a comparatively inexpensive form of spectrometer which has sufficient accuracy for ordinary purposes in a physiological laboratory. S. S. Z.

Spark Spectra of Various Elements in Helium in the Extreme Ultraviolet. J. C. MCLENNAN and A. C. LEWIS (*Proc. Roy. Soc.*, 1920, [*A*], **98**, 109—114).—The new wave-lengths 1745 Å.U., 1742·5 Å.U., and 1657 Å.U., have been observed in the spectrum of silicon. The spectra of tellurium, molybdenum, and zirconium were examined, and the results tabulated. These are considered to be correct to 0·5 Å.U. A strong doublet appears common to all the spectra in the neighbourhood of 1745 Å.U., probably due, according to Lyman, to silicon. A strong line at 1656·7 Å.U. was found on all the plates, which Lyman gives as present in all metallic spark spectra in helium. It was probably due to carbon from the decomposition of carbon monoxide given off from the wax joint. In the spectra of molybdenum and zirconium all the wave-lengths observed were of weak intensity. The radiations from tellurium were stronger, and their relative intensities are given in the table. A reproduction of the spectrum of this element is given. J. R. P.

Arc Spectra in Vacuum and Spark Spectra in Helium of Various Elements. J. C. MCLENNAN, J. F. T. YOUNG, and H. J. C. IRETON (*Proc. Roy. Soc.*, 1920, [*A*], **98**, 95—108. Compare A., ii, 458, 459).—The vacuum arc spectra of antimony, bismuth, calcium, magnesium, selenium, silver, and copper, and the spark

spectra in helium of antimony, bismuth, cadmium, lead, magne ium, thallium, and tin, have been investigated in the region belo 1850 Å.U. The work with the vacuum grating spectrograph ha resulted in the extension of the vacuum arc spectrum of copper t about 1216 Å.U. J. R. P.

Air Lines in Spark Spectra from λ 5927 to λ 871 PAUL W. MERRILL (*Astrophys. J.*, 1920, **51**, 236—243).—In obser ing the spectrum of any element, if the source is the spark in ai there are a large number of lines due to the air itself, which it impossible to eliminate. In order to be able to distinguish th lines due to the various components of the atmosphere, the auth has observed the spark in air and in oxygen, using several differe elements as electrodes. The wave-lengths of 58 air lines are giv in a table. Because of the ill-defined nature of these lines, t accuracy is not very great. Twenty of the list correspond wi known lines of hydrogen, nitrogen, oxygen, or argon, including s lines of the red spectrum of argon and four of oxygen lines whi had not previously been observed in spark spectra. Two others a probably due to oxygen; the rest have not as yet been identifie All the identified lines are found to be shifted toward the r with respect to vacuum tube wave-lengths. This increase in wa length amounts to about 0·1 Å. for the oxygen lines, 0·6 Å. f the argon lines, 0·7 Å. for the hydrogen α-line, and varies fr 0·1 Å. to 0·7 Å. for the nitrogen lines. On introducing self-ind tion the only marked change is the weakening of the nitrogen li λλ 6482 and 6610. Using as source the condensed spark in an atn sphere of commercial oxygen, several identifications of oxygen a nitrogen lines previously observed in the vacuum tube we confirmed, and the doubtful identification of λ 7157 as due oxygen is strengthened. CHEMICAL ABSTRACTS.

Vacuum Grating Spectroscopy. J. C. MCLENNAN (*Pr Roy. Soc.*, 1920, [*A*], **98**, 114—123).—It would appear that in t spectroscopy of the ultraviolet the procedure to be followed whi would permit of the most rapid progress being made would be, far as emission spectra are concerned, to work with a vacu grating spectrograph and to use an atmosphere of helium. The is evidence to show that this gas is transparent to wave-lengths short as 400 to 500 Å.U., or even shorter. As regards absorpti spectra, it is shown that if a vacuum grating spectrograph, p vided with a lamp of the "Pointolite" type, is filled with heli to a suitable pressure, arcs can be struck in the gas, when t requisite voltages are applied, which will provide a radiation co sisting of wave-lengths extending probably near to 400 Å.U. interposing vapours of elements between the arc and the grati of the spectrograph, it should be possible to obtain the absorpti spectra of the elements vaporised. An improved apparatus described, and preliminary measurements made down to 102 Å.U., although indications were obtained on all the plates of

faint continuous spectrum extending to well below 500 A.U. The potential fall between the electrodes was only 45 volts. J. R. P.

Existence of a Relation between the Heads of Banded Spectra. TOKIHARU OKAYA (*Proc. Phys. Math. Soc. Japan*, 1919, [3], 1, 332—343. Compare this vol., ii, 140).—The relations $\lambda/\lambda' = \sqrt{m/m'}(p/q)^{3/2}$ and $p/q = a/a'$ between the heads of bands due to different elements of the same group in the periodic system, where λ and λ' are the wave-lengths of the heads of the bands, m and m' the atomic weights, p and q integers smaller than ten, and a and a' the radii of the atomic models of Nagaoka, are open to the criticism that there are so many heads in the spectra of the gold group and the alkaline earth group examined previously that the above relations may have been due to chance. In the present paper, by choosing elements the spectra of which have few heads, such as palladium and nickel, it is shown that the above relations hold only for elements in the same group, and do not hold for elements of different groups. Other elements for which the relations hold are vanadium, columbium, and tantalum. The conclusion is drawn that the oxide of vanadium at the moment of emission of band spectra assumes the form VO_2 and not V_2O_5, which is the form stable at ordinary temperatures.

CHEMICAL ABSTRACTS.

Fluorescence of the Uranyl Salts. EDWARD L. NICHOLS, HORACE L. HOWES, ERNEST MERRITT, D. T. WILBER, and FRANCES G. WICK (*Carnegie Inst. Washington Publication*, 1919, **298**, —241).—The historical introduction is followed by chapters devoted to: structure of fluorescence spectra; preliminary observations on certain uranyl salts; phosphorescence of the uranyl salts; ultimate structure on cooling to $-185°$; polarised spectra of double chlorides; the nitrates and phosphates, water of crystallisation, crystalline form; the acetates; the sulphates; and frozen solutions. Since the fluorescence of certain uranyl compounds is resolved into groups of narrow line-like bands when these compounds are excited to luminescence at very low temperatures, a study of the fluorescence has been undertaken. The spectra of numerous uranyl salts have been mapped. Owing to the extraordinarily complex character of the phenomena, no satisfactory theory has as yet been evolved, but the mass of facts recorded and the general principles established will, it is hoped, afford a basis for the successful theoretical development of this important and little understood branch of the science of radiation. Appendices are devoted to the chemistry and crystallography of the uranyl salts, and to the subject of phosphoroscopes. CHEMICAL ABSTRACTS.

Optical Rotation, Optical Isomerism, and the Ring Electron. H. STANLEY ALLEN (*Phil. Mag.*, 1920, [vi], **40**, 426—439).—A theoretical paper in which an hypothesis of optical rotation is advanced in which the electron, instead of being

regarded as a point charge, is looked on as an anchor ring of negative electricity rotating rapidly about its axis as suggested by Parson (Smithsonian Misc. Coll., No. 2371, Nov., 1915). Such a ring electron vibrating in a linear path takes the place of an ordinary electron moving in a spiral path as postulated by Drude. It is shown that a rotation of the plane of polarisation of light will result, and an expression is found for the amount of rotation per unit length. Employing the theory of atomic structure due to Lewis and Langmuir (A., 1916, ii, 310; 1919, ii, 328), a graphical representation may be obtained for the dextro- and lævo-rotatory forms of a compound. The experimental facts with regard to optical activity are in good agreement with the hypothesis put forward, which may be applied not merely to carbon compounds, but to any compound containing an asymmetric atom. On the assumptions made it is possible to deduce that eight isomerides of cinnamic acid may exist. J. F. S.

Influence of Constitution on the Rotation of Optically-active Substances. XI. Normal and Abnormal Rotation Dispersion and its Calculation. H. Rupe and Arthur Akermann (*Annalen*, 1920, **420**, 1—32. Compare A., 1917, i, 539, and previous abstracts).—An examination of more than fifty dispersion curves leads the authors to the conclusion that the normal rotatory dispersion of organic substances can be expressed by the simple formula $\alpha_n = K_0/\lambda_n^2 - \lambda_0^2$, in which K is the "rotation constant" and λ_0^2 is the dispersion constant; the expression has been used previously by Lowry and Dickson (T., 1915, **107**, 1173). The formula is shown to be applicable to liquids in substance and in solution; it gives results which are in good harmony with the observed data over the visible spectrum, and can probably be also employed outside these limits.

In previous communications, Rupe has endeavoured to distinguish between normal and abnormal rotatory dispersion on the basis of the displacement of the "characteristic wave-length"; it now appears that when a substance exhibits abnormal dispersion within the region of measurement, the characteristic wave-length differs from the mean of the respective class of compounds, but, although strong displacement is necessary for abnormal dispersion, it is not by itself sufficient.

The methods of calculating the values of K_0 and λ_0^2 are fully discussed, and it is shown that, provided the dispersion is normal, the calculated values for the specific rotations of a large number of compounds for a given wave-length agree with the values observed within the limits of experimental error. The following criteria of abnormal dispersion are then deduced, in which three types are distinguished: (i) Apparently normal rotatory dispersion with greatly displaced dispersion curve; the divergence between the calculated and observed values does not amount to more than three times the mean experimental error, but λ_0^2 and λ_s differ markedly from the mean value for the appropriate class of compound.

ii) Relative abnormal rotatory dispersion, in which the differences re from three to five times as great as the mean experimental rror; and (iii) Total abnormal rotatory dispersion, in which the ifferences exceed fifteen times the mean experimental error.

The connexion between optical activity and constitution is disussed at length, and it is pointed out that comparisons between iolecular rotations observed with a single wave-length are inadeuate for the elucidation of the problem, and that the rotatory ispersion must also be ascertained. The latter is greatly influnced by the solvent used, and, at present, this action does not ppear to be exerted in any regular manner even towards subances of the same type. The influence of constitution on K_m is escribed, and it is found that if the added radicle is an aliphatic turated hydrocarbon group and if the chemical change does not ivolve any considerable change in the optical properties of the ymmetric complex, K_m remains approximately constant in homogous series. The rule also applies when aromatic groups are itroduced, provided that at least one methylene group lies between ie aromatic radicle and the asymmetric complex. K_m is increased the introduction of one or more ethylenic linkings, by a triple nd (the effect of this is noticeably less than that of two double nds), and by the direct attachment of an aromatic nucleus to the ymmetric complex. Changes in K_m are also induced by one or ore groups containing oxygen. It thus appears that K_m is not fected by the number of groups required to form the molecule, it is mainly dependent on the spatial distribution of the atoms d the relative distances from one another. H. W.

Activation of Photochemical Elements with Silver aloid Electrodes and their Application. SATOYASU IIMORI d TOSHIMASA TAKEBE (*J. Tokyo Chem. Soc.*, 1920, **41**, 77—185). The mechanism and sensitisation of the Becquerel effect and the plication of the photochemical cell for measuring candle-power e extensively considered. In order to obtain the most stable aximal photovoltaic effect the silver haloid electrodes are prepared follows: A small silver plate is soaked in haloids of iron, copper, ercury, or thallium; later its surface is freed from the solutions use of suitable solvents, and it is placed in a solution of iodine alcohol, benzene, chloroform, or ether. The final coating of the ectrodes with iodide is perfected by placing them in 0·3—5 -potassium iodide saturated with silver iodide. Such an electrode, ter several days, becomes exceedingly sensitive, and contains a rmanent film. Proper concentration of potassium iodide is very portant. The cells of 20 c.c. and 90 c.c. capacity are made of ss, with ebonite covers. The outer surface is covered with tin l except the window, which admits the light and behind which e of the electrodes is placed. A solution of potassium iodide is o used for the cell. The *E.M.F.* is measured by Poggendorff's thod, the Weston cell being used as standard. Several factors obtaining maximal photovoltaic effect are studied. The effect of

concentration of the cell liquid is expressed by $\pi_m = A + B \log 1/C$, in which π_m is in millivolts, C = concentration of potassium iodide, A and B are constants due to temperature, degrees of illumination, electrodes, etc. Rise of temperature lowers the effect, its extent depending on the illumination and characters of the cell. The effect of intensity of illumination is expressed by $\pi_m = \sigma(1 - e^{-KE_a})$, where E is the intensity; σ, K, and a are constants for cells, temperature, and wave-length. For a limited condition, a much simpler formula, $\pi_m = a \log E - b$, can be used. The effect of the size of windows is given by $\pi_m = \rho(1 - e^{-hA\beta})$, where A = area of window, which is always smaller than that of the electrode, and ρ, h, and β are constants. The time required to attain the maximal effect is greater with rise of temperature and concentration of potassium iodide, and smaller with increase of illumination and size of the window. The time required to decrease to the half of the maximal value after the light is removed is greater with the larger concentration of the liquid, but is independent of the intensity of illumination and the size of the window. Theoretical explanations for all factors are given. Considering the effect of temperature and nature and concentrations of the liquid used for the battery, it is concluded that the photovoltaic effect produced with haloid electrodes must be caused by reversible chemical reaction of the silver iodide, which takes place in the following order: at the exposed electrode $mn\,AgI \longrightarrow mn\,Ag + mn\,I$, $mn\,I \longrightarrow m\,I'n + m\oplus$ becoming $\oplus$; at the unexposed electrode, $mn\,AgI \longrightarrow mn\,Ag + m\,I'n + m\oplus$, $mn\,AgI + m\,I'n \longrightarrow mn\,AgI + m\ominus$, $mn\,AgI \longrightarrow mn\,AgI + m\oplus\ \ominus$, $\oplus\ominus = 96540$ coulombs. CHEMICAL ABSTRACTS.

The Mechanism of Chemical Actions Provoked by *X*-rays. A. DAUVILLIER (*Compt. rend.*, 1920, **171**, 627—629).—The mechanism suggested is that the cause of the chemical action is the destruction of the negative ions, which alone can lose their electrons by the impact of the rapid electrons constituting the corpuscular radiation. The corpuscles, slowly expelled, neutralise the adjacent positive ions, the electronegative and electropositive elements thus being liberated in the atomic state. These produce colorations in solid or viscous substances and chemical changes in media where they are mobile. Several reactions are examined in the light of this hypothesis. W. G.

Explanation of Röntgen Spectra and the Constitution of Atoms. ADOLF SMEKAL (*Physikal. Zeitsch.*, 1920, **21**, 505—506).—The theories of Vegard (A., 1919, ii, 129) and of Kroo (A., 1918, ii, 303) are discussed. The calculations of Vegard do not do justice to the most exact measurements of Siegbahn (A., 1919, ii, 261), whereas the formula of Kroo appears to apply with great accuracy. The conclusions of Vegard as to the structure of atoms are thereby vitiated. J. R. P.

The *X*-ray Absorption Spectra of Phosphorus. J. BERGENGREN (*Compt. rend.*, 1920, **171**, 624—626).—In th

X-ray absorption spectra of the different varieties of phosphorus, the author finds that the wave-lengths of the limits of absorption are different for black phosphorus and for phosphorus in the form of phosphoric acid. That of red phosphorus shows a double limit, one component of which is identical with that of black phosphorus, and the other, attributed to yellow phosphorus, coincides, at least approximately, with that of phosphoric acid. W. G.

The Fine Structure of the Discontinuities of Absorption in *X*-ray Spectra. M. DE BROGLIE and A. DAUVILLIER (*Compt. rend.*, 1920, **171**, 626—627).—A discussion of Kossel's work (compare *Zeitsch. Physik*, 1920, **1**, 119) in the light of Bergengren's work on phosphorus (compare preceding abstract).

W. G.

Precision Measurements in the *K*-series of *X*-rays. Elements from Copper to Sodium. ELIS HJALMAR (*Zeitsch. Physik*, 1920, **1**, 439—458).—Siegbahn's vacuum spectrograph has been used in making wave-length measurements. Several new weak lines are found, besides the component of β predicted by Sommerfeld. These are: one in the neighbourhood of β, a close doublet of shorter wave-length than $\alpha_3\alpha_4$, and a line between α_1 and α_3. Not all these occur in any one element. The relation $n\lambda = 2d \sin \phi$ is tested by comparing the angle of reflection of the same line in different orders. The lattice constant for gypsum is measured as $\log 2d = 1{\cdot}1805620{-}8(\pm 0{\cdot}0000149)$.

CHEMICAL ABSTRACTS.

Origin of the Iodine Band Spectrum and its Place in the Quantum Theory. W. STEUDING (*Zeitsch. Physik*, 1920, **1**, 426—430).—The iodine band spectrum results from neutralisation of the ionised atoms and their combination to form the molecule. The high frequency limit of the spectrum gives, on the quantum theory, the work necessary for the decomposition from molecules to ions. This has been calculated by Born (A., 1919, ii, 214) on the space-lattice theory, and the agreement is quantitative. CHEMICAL ABSTRACTS.

Fine Structure of the Near Infra-red Absorption Bands of the Halogen Acids. WALTER F. COLBY (*Astrophys. J.*, 1920, **51**, 230—235).—A quantum theory of the fine structure in the infra-red absorption spectra of the diatomic gases is put forward. The postulate of Bjerrum (*Nernst Festschrift*, 1912, 90), that the fine structure of these bands is due to the rotation of the molecules in stationary states corresponding with the quantum relation, has proved very fruitful. The present paper proposes to test the hypothesis by comparing the theoretical results for the simplest molecule model of the Bohr type with the experimental results recently obtained by Imes (*Astrophys. J.*, 1919, **50**, 251) for the halogen acids. For hydrogen fluoride, chloride, and bromide, the observed interatomic vibration frequencies are

respectively 38, 40, and 47% less than the theoretical, whilst the computed separations of the pairs of nuclei are, respectively, 38, 54, and 59% less than the values given by Imes. The variation with mass is explained as a screening effect which has been neglected in the elementary theory. The agreement between theory and experiment is sufficient to lend support to the Bjerrum hypothesis, and suggests the importance of developing a more adequate theory involving fewer simplifying assumptions.

CHEMICAL ABSTRACTS.

Structure of the Helium Atom. IRVING LANGMUIR (*Science*, 1920, **51**, 605—607).—The ionisation potential as calculated from Bohr's theory, 28·8 volts, does not agree with the experimental value, 25·4 volts. By means of Landé's theory of the transference of momentum from one electron to another around the nucleus rather than a rotation of the electrons themselves, the author has calculated the numerical dimensions of the path of the electrons in the helium atom after four approximations to within 0·1%. Each electron travels through less than half an orbit when it is reflected back on approaching the other electron.

CHEMICAL ABSTRACTS.

Helium and Parhelium. J. FRANCK and F. REICHE (*Zeitsch. Physik*, 1920, **1**, 154—160).—There are two separate systems of spectral series for helium which belong to helium and to parhelium. In helinm the electron orbits are coplanar, whilst in parhelium they are at an angle to each other, as described by Landé. Parhelium is the less stable, and its ionisation potential is the one determined experimentally. The base line for the principal series for helium is 10,830 Å. and for parhelium is 20,582 Å., and is caused by the return, in each case, to a diquantal orbit. For normal helium, that is, uniquantal, the resonance potential, in agreement with the calculations of Landé, would lead to a ground line of about 600 Å. A change from a higher quantum orbit of one system to a lower of the other never occurs. Parhelium is the normal condition of the element (uniquantal).

CHEMICAL ABSTRACTS.

Aggregate Recoil during the Decomposition of α-Radiating Substances. ROBERT W. LAWSON (*Wien Anz.*, 1919, 86—88; from *Chem. Zentr.*, 1920, iii, 431).—It has been observed repeatedly that polonium which has been deposited electrolytically on metallic foil activates objects in its immediate vicinity. The following explanation of the phenomenon is advanced. The polonium lies on the metallic support in aggregates of atoms. When an α-particle is discharged from such an aggregate, the latter receives the recoil in the opposite direction and leaves the support. The author designates the phenomenon "aggregate recoil," and examines its dependence on the nature of the supporting metal and on the prevalent gas pressure. The importance of the recoil on the estimation of the life period of polonium is discussed.

H. W.

Rapid Graphic Method of Estimating Radium. N. E. DORSEY (*Physical Rev.*, 1919, **14**, 173; from *Chem. Zentr.*, 1920, iii, 399).—The increase in the γ-radiation of a radium preparation from the time t_1 to t_2 is denoted by the expression $J_2 - J_1 = 1{\cdot}0089 \,.\, e^{-\lambda t_1}(1 - e^{-\lambda(t_2 - t_1)}) \,.\, J_\infty$, where λ is the rate of decay of the emanation and J_∞ the equilibrium value. If the observed values of J are plotted against $(1 - e^{\lambda t})$, in which t is calculated from any desired instant, a straight line is obtained, the intersection of which with the ordinate for $t = \infty$ gives the equilibrium value J_∞, which can thus be graphically determined. H. W.

Radium Content of the Rocks of the Loetschberg Tunnel. J. H. J. POOLE (*Phil. Mag.*, 1920, [vi], **40**, 466—471).—The radium constant of 82 specimens of rocks collected at different points in the Loetschberg Tunnel has been estimated by the fusion method. The content is found to be fairly constant throughout the whole length, a mean value $2{\cdot}2 \times 10^{-12}$ grams per gram of rock being obtained. This value is obtained from values lying between $0{\cdot}8 \times 10^{-12}$ from a talc schist obtained 480 m. from the south end of the tunnel, and $6{\cdot}5 \times 10^{-12}$ from a felspar talc schist obtained 395 m. from the south end. For individual rocks, the following mean values were obtained: granite (7 specimens), $2{\cdot}3 \times 10^{-12}$; limestone (16 specimens), $1{\cdot}5 \times 10^{-12}$; talc schist (16 specimens), $2{\cdot}0 \times 10^{-12}$; quartz schist (12 specimens), $2{\cdot}4 \times 10^{-12}$; mica schist (2 specimens), $2{\cdot}1 \times 10^{-12}$; hornblende schist (2 specimens), $3{\cdot}1 \times 10^{-12}$; schist lustré (2 specimens), $3{\cdot}4 \times 10^{-12}$; felspathic schist (3 specimens), $2{\cdot}7 \times 10^{-12}$; unclassified schists (16 specimens), $2{\cdot}5 \times 10^{-12}$; aplite (2 specimens), $2{\cdot}5 \times 10^{-12}$; quartz porphyry (1 specimen), $2{\cdot}5 \times 10^{-12}$; anhydrite (2 specimens), $1{\cdot}1 \times 10^{-12}$; and quartz sandstone (1 specimen), $4{\cdot}3 \times 10^{-12}$. The mean radium constant of 53 schists is $2{\cdot}4 \times 10^{-12}$ grams per gram of rock. J. F. S.

Atmospheric Electricity. LXI. Measurement of the Radium Emanation Content of the Air at Innsbruck. RELY ZLATAROVIC (*Wien Anz.*, 1920, 75; from *Chem. Zentr.*, 1920, iii, 334).—By the use of charcoal and petroleum as absorbents, an ionisation vessel which previously showed a saturation current, i_1, was completely freed from emanation; the saturation current, i_2, which was now measured, was found to be constant. The difference, $i_1 - i_2$, is applied to the calculation of the emanation content, and, as a mean of forty-nine observations, gives the value 433×10^{-18} Curie/c.c., the extreme values being 1110 and 40. Dependence on meteorological factors could only be so far recognised in that rainy periods correspond with lower emanation values. H. W.

Effects of Electron Collisions with Atmospheric Neon. FRANK HORTON and ANN CATHERINE DAVIES (*Proc. Roy. Soc.*, 1920, [*A*], **98**, 124—146).—The minimum radiation velocity was found to be 11·8 volts with neon at an average pressure of 0·133 mm.

The minimum ionisation velocity was found to be 16·7 volts. The second radiation velocity was found to be 17·8 volts. The second and third ionisation velocities were found to be 20·0 and 22·8 volts respectively. The existence of three critical ionisation velocities and two critical radiation velocities indicates that neon differs more in constitution from helium and argon than would be expected from its position in the table of the elements. The accepted view of the connexion between the quantities of energy required for the production of radiation and of ionisation is that they correspond with the first and with the limiting frequency, respectively, of some particular spectral series of the element concerned. On this view, it would be expected that with every ionisation velocity there would be associated a definite radiation velocity. In the experiments, evidence of three ionisation velocities, but of only two radiation velocities, was obtained. The two radiation velocities may occur so close together that they do not give separate indications on the curves, in which case one might escape detection. Another possibility is that the ionisation observed at one of the three critical velocities is a spurious effect. The minimum radiation velocity of helium is 20·4 volts, close to the value 20·0 volts found above. The radiation velocity of 11·8 volts appears to be associated with the ionisation velocity of 16·7 volts, and the radiation velocity of 17·8 volts with the ionisation velocity of 22·8 volts. If neon consists of two or more constituents having different radiation and ionisation velocities, the critical velocities 11·8 and 16·7 are to be attributed to one, and the values 17·8 and 22·8 to the other. J. R. P.

Constancy of the Ratio of Actinium to Uranium in Natural Minerals. STEFAN MEYER and VIKTOR F. HESS (*Sitzungsber. K. Akad. Wiss. Wien*, 1919, **128**, [2*a*], 909—924; from *Chem. Zentr.*, 1920, iii, 435—436).—It has been assumed for a long time that the actinium series is derived by indirect degradation of the uranium–radium series. If this is the case, the ratio of actinium to uranium or radium must be constant in all uranium minerals. Few, and not very concordant, observations have been recorded, chiefly by Boltwood, in this connexion. The authors have therefore examined exhaustively the reputed constancy of the ratio Ac:U, and have used uranium minerals which differ as widely as possible from one another, both in origin and composition, and include the following: amorphous Joachimsthal pitchblende, crystalline pitchblende from Morogoro, bröggerite, and two different specimens of thorianite. Quantities of the minerals corresponding with 30 grams of uranium were dissolved in concentrated nitric acid, and the solutions were diluted with water to 1 litre and brought into rotating flasks; the radium emanation was first removed in a constant current of air and, immediately afterwards, the active precipitate of actinium (with a portion of thorium precipitate if present) was collected on a negatively charged plate. The value of Ac-$B+C$ could be readily derived from the known half life-periods for Ac-$B+C$ and

Th-$B+C$. The observed activities are not great, but the results of repeated measurements are quite concordant. The ratio Ac : U is found to be constant in all minerals, thus giving a sure support for the hypothesis that the actinium series is genetically related to uranium. H. W.

Ionisation in the Solar Chromosphere. MEGH NAD SAHA (*Phil. Mag.*, 1920, [vi], **40**, 472—488).—From a discussion of the high-level chromospheric spectrum, it is shown that this region is mainly composed of ions of calcium, barium, strontium, scandium, titanium, and iron, whilst in the lower layers both ions and atoms occur. An attempt is made to account for these facts from the point of view of Nernst's theorem of the reaction isobar, by assuming that the ionisation is a type of reversible chemical process taking place according to the equation $Ca \rightleftharpoons Ca^{+} + e - U$. The energy of ionisation, U, can be calculated from the ionisation potential of the elements. For the determination of the chemical constant and the specific heat, the electron is assumed to be a monatomic gas with an atomic weight 1/1836. The equation shows the great influence of pressure on the relative degree of ionisation. The almost complete ionisation of calcium, barium, and strontium in the high-level chromosphere is due to the low pressure in these regions. The calculated values are in good agreement with the experimental values of King (*Astrophys. J.*, **48**, 13). Hydrogen is completely dissociated into atoms at all points in the solar atmosphere. It is also shown that the greater the ionisation potential of an element, the less readily does ionisation occur under a thermal stimulus. Calculations have been made in the case of hydrogen ($V=13{\cdot}6$ volts) and helium ($20{\cdot}5$ volts) which show that these elements are not ionised to an appreciable extent anywhere in the sun. Helium is ionised only in stars of the highest temperature (>16000° K), which therefore alone can show the Rydberg line 4686 and the Pickering lines $\nu=N[1/2^2-1/(1+1/2)^2]$.

J. F. S.

Relative Ionisation Potentials of Gases as Observed in Thermionic Valves. G. STEAD and B. S. GOSSLING (*Phil. Mag.*, 1920, [vi], **40**, 413—425).—A method is described whereby the ionisation potential of gases may be determined. This method consists in determining the differences of potential which are necessary for the production of positive ions in soft thermionic valves. The tube used was a three-electrode valve of the usual form, the cold electrodes being connected together. Next to the tungsten filament there was a molybdenum spiral, 0·4 mm. diam., coiled into a helix of 4·5 mm. diam., and having four to five turns per cm. Outside this was a nickel cylinder 10 mm. diam. When an appreciable quantity of a gas is present in such a tube, the voltage-current curve changes, at a definite potential, from the high vacuum characteristic. This point represents the beginning of the emission of positive ions and gives the ionisation potential of the gas. Experiments have been carried out with mercury

vapour, argon, hydrogen, carbon monoxide, nitrogen, and helium at several pressures, and the following values found for the ionisation potential: mercury, 10·8 volts; argon, 12·5 volts; hydrogen, 15·0 volts; carbon monoxide, 15·0 volts; nitrogen, 17·2 volts; and helium, 20·8 volts. The value obtained for carbon monoxide differs from that obtained by other observers, and it is suggested that this does not represent a true ionisation potential, but rather a photoelectric effect. The present method of work is not open to the criticism offered to most methods of determining ionisation potentials. J. F. S

Effect of a Trace of Impurity on the Measurement of the Ionisation Velocity for Electrons in Helium. FRANK HORTON and DORIS BAILEY (*Phil. Mag.*, 1920, [vi], **40**, 440—450). —The ionisation potential of helium has been redetermined with perfectly pure gas and the effect of impurities on this value investigated. The results emphasise the importance of maintaining the helium perfectly pure when investigating the ionisation of gas by electron collisions. The only satisfactory method when a glass apparatus is used is to have a slow circulation of freshly purified helium through the ionisation chamber during the experiments. It is possible that if fused silica were substituted for glass, contamination of the gas would be less likely to occur. The ionisation curves indicate that the minimum ionisation velocity for electrons in helium is 25·0 volts, a value rather lower than that obtained by Horton and Davis (A., 1919, ii, 210). The present results also indicate that the minimum radiation velocity for electrons in helium is 21 volts; but this value is no doubt too high, for the point at which ionisation of the impurities by the helium radiation was detected depended on the amount of impurity present, and was probably always higher than the point at which radiation was first produced from the helium atoms. J. F. S.

Ionisation Potential of Hydrochloric Acid and the Electron Affinity of Chlorine. PAUL D. FOOTE and F. L. MOHLER (*J. Amer. Chem. Soc.*, 1920, **42**, 1832—1839).—The experiments indicate that the collision of an electron of sufficient velocity with a molecule of hydrogen chloride results in the *immediate production* of a positively charged atom of hydrogen and a negatively charged atom of chlorine. The ionisation causes disruption of the bond between the two ions in the molecule. The work necessary to ionise a gram-molecule of hydrogen chloride is accordingly the work of ionising a gram-atom of hydrogen plus the heat of formation of hydrogen chloride plus the heat of dissociation of 0·5 gram-molecule of chlorine minus the electron affinity of a gram-atom of chlorine. This, expressed in volts and referred to a single molecule, is 13·7 volts, in excellent agreement with the experimentally determined value, 14·0 volts. The electron affinity of chlorine is calculated as 4·8 volts. Hydrogen chloride is not known to possess any characteristic visible or ultraviolet

spectrum, in agreement with the observed peculiar type of ionisation and the absence of a resonance potential. Any radiation emitted which is characteristic of hydrogen chloride would be produced by the union of the hydrogen ion and the chlorine ion, giving rise to a quantum of $h\nu = eV$, where $V = 14 \cdot 0$ volts. The corresponding wave-length in the extreme ultraviolet is $\lambda = 880$ A.U., which could be observed, though with difficulty. A high voltage discharge through hydrogen chloride shows the ordinary spectrum of hydrogen. The attraction between a hydrogen nucleus and a halogen atom is about the same as the interaction between a hydrogen nucleus and the electron in the neutral hydrogen atom, as predicted by Haber. J. R. P.

Ionisation Potentials of Argon, Nitrogen, Carbon Monoxide, Helium, Hydrogen, and Mercury and Iodine Vapours. Clifton G. Found (*Physical Rev.*, 1920, **15**, 132—133). —The object was to determine the effect of gas on the volt-ampere characteristics of a two-electrode electron discharge tube, and to determine the voltage at which the gas affected the space charge of the tube or ionisation potential. By the use of a commutator, the heating circuit along the filament was broken while the space current was measured, so that the current, $i = A(V - V_0)^{3/2}$, where V_0 is the voltage equivalent to the initial velocity of the ions. The ionisation potential for argon was 15—16 volts at 1—200 bars pressure. With increase in filament temperature, due to the increased V_0, the potential was lowered. Nitrogen gave about 16 volts, carbon monoxide 13·5—14, mercury vapour 10—11, iodine vapour 8·5, whilst the values 20·5 for helium and 15 for hydrogen were uncertain. Chemical Abstracts.

Ionisation Potential of Mercury Vapour as a Function of the Temperature of the Cathode. T. C. Hebb (*Physical Rev.*, 1920, **15**, 130).—Values as low as 3·2 volts were obtained for the ionisation potential of mercury vapour at very high temperatures. The striking voltage, $V = 10 \cdot 5 - 0 \cdot 002T$, where T is the absolute temperature. Chemical Abstracts.

Ignition of Gases at Reduced Pressures by Transient Arcs. W. M. Thornton (*Phil. Mag.*, 1920, [vi], **40**, 450—460).—The ignition of hydrogen, methane, ethane, pentane, propane, carbon monoxide, and coal gas by both direct- and alternating-current arcs has been investigated at a number of reduced pressures. The ignition current is plotted against the pressure, and curves produced in all cases. With direct-current arcs, the ignition current falls rapidly to a minimum with increase in pressure, and then rises equally rapidly to a maximum, after which it falls slowly to a constant value. The lower limit is found in all cases at about 0·2 atm., whilst the rapid rise lies between 0·4 and 0·5 atm. A mean ordinate (current in amperes) lies at the points:

hydrogen 0·30 ampere, methane 1·20 amperes, ethane 1·12 ampere propane 0·87 ampere, and pentane 0·66 ampere, and these mea values may be expressed by the equation $i = 0{\cdot}334 + 23{\cdot}5/mol.$ w The relative influence of hydrogen and carbon on the inflamma bility of the hydrocarbons is given by the equation

$$(i - i_0) = an_C/(n_H)^2,$$

where i is the ignition current of the hydrocarbon, i_0 that hydrogen, a a constant, n_C and n_H, respectively, the number carbon and hydrogen atoms. Two causes effect ignition, a therm cause and an ionisation cause; either of these causes may be pr dominant, depending on conditions, and the form of the igniti curve depends on which of these causes is operative. With alter ating current, the form of the curves is very much changed; the case of hydrogen, the curve falls rapidly to 0·23 ampere, an then rises to 0·26 ampere, after which it falls to a steady value about 0·1 ampere. With methane, there is only the slighte tendency for the curve to rise after the preliminary fall, but the is a halt, and then a slower fall to a stationary value. In th case of ethane and propane, the curve is of the same shape as th of methane, but the flat halt is very much longer. Coal gas about ten times as inflammable as carbon monoxide. The whc of the curves given are reminiscent of the critical gas isothermal

J. F. S.

Electrolysis of Solutions of Sodium Nitrite using a Silv Anode. F. H. JEFFERY (*Trans. Faraday Soc.*, 1920, **15**, 16—20). The reactions at the anode during the electrolysis of solutions sodium nitrite of different concentrations in a divided cell, with silver anode and platinum cathode, were investigated. In no ca was silver deposited on the cathode. Silver dissolved from t anode, no gas being evolved. A deposit formed on the ano which was found to be silver nitrite, together with a small p centage of finely divided silver from the disintegration of t anode. Measurements of the anode potential were made, and t results showed that in the immediate neighbourhood of the anc the concentration of silver ions was not increased by the nitr ions. A complex salt, $NaAg(NO_2)_2$, was isolated at the anode small, well-shaped, bright yellow crystals by electrolysing an anol of 50 grams of sodium nitrite in 100 grams of water for fifty- hours with a current of 0·072 ampere. The solution was allo to evaporate isothermally over concentrated sulphuric acid in exhausted desiccator. Further evaporation led to the separat of a mixture of this salt and sodium nitrite. J. R. P

Transference Numbers of Sodium and Potassium Mixed Chloride Solutions. S. A. BRALEY and J. LOWE H (*J. Amer. Chem. Soc.*, 1920, **42**, 1770—1776).—Over a range total concentration from $0{\cdot}2N$ to $1{\cdot}6N$ with equivalent amount sodium and potassium chlorides, a relatively greater amount sodium is transferred than is indicated by calculation from conductance of the simple salt solutions, on the basis of the

hydric principle. The increase of sodium transferred over this range of concentration is, roughly, a linear function of the total salt concentration. The results are in harmony with those of Smith and Ball (A., 1917, ii, 247), and may be explained on the basis of complex formation, the simplest form of which may be expressed in the form $NaCl + KCl \rightleftharpoons Na(KCl_2) \rightarrow Na^{\cdot} + KCl'_2$.

J. R. P.

Dependence of Electro-osmosis on the Chemical Properties of the Diaphragm. STANISLAW GLIXELLI (*Anzeiger Akad. Wiss. Krakau*, 1917, [*A*], 102—128; from *Chem. Zentr.*, 1920, iii, 431).—The fundamental assumption in the theory of electro-osmosis is that the potential of the mobile layer of liquid, ϕ_1, differs from the potential, ϕ_0, of the layer attached to the wall of the diaphragm. A proportionality exists between the difference of potential ($\phi_1 - \phi_0$) of the electrical double layer and the rate of electro-osmosis or cataphoresis. The causes of the difference of potential and the mechanism of the phenomenon of the charge in the electrical double layer are discussed. All that is known is that the electrical double layer is considerably influenced by the addition of electrolytes, more particularly by hydrogen and multivalent ions and by the cations of the heavy metals and complex organic bases, and that the positively charged diaphragms are discharged by anions and the negatively charged ones by cations. The methods previously adopted have not permitted the use of moderately concentrated electrolytes. The author has elaborated a method of observing and approximately measuring the velocity of electro-osmosis which is particularly adapted to the estimation of the isoelectric point; it can be used with gels and powders, and permits the employment of approximately $0.5N$-solutions of electrolytes. The influence of hydrogen and hydroxyl ions on the electric charge of the following inorganic gels has been examined: silicic and tungstic acids, antimonic anhydride, stannic and titanic acids, glucinum oxide and hydroxide, zinc, iron, magnesium, and silver oxides, and nickel hydroxide. With some of these, the concentration of hydrogen and hydroxyl ions at the isoelectric point is determined; with others, the lower limit of its value is ascertained. With regard to the hydrogen-ion concentration at the isoelectric point, the substances examined fall into four distinct groups: acids, acid ampholytes, basic ampholytes, and bases. The results of the investigation are examined in the light of the present theories of the origin of the electric charge in colloid particles.

H. W.

Specific Heat of Liquids at Constant Volume. K. ZAKRZEWSKI (*Anzeiger Akad. Wiss. Krakau*, 1917, [*A*], 86—101; from *Chem. Zentr.*, 1920, iii, 440).—The values for $(\partial p/dt)_v = a/\mu$ are calculated from the measurements of Seitz and Lechner (A., 1916, ii, 174). Whilst these values for ethyl alcohol at different temperatures between 0° and −90° lie with sufficient accuracy on a straight line in the $\partial p/\partial t$ volume diagram, for

ethyl ether and carbon disulphide they lie on different lines which are parallel to one another. Within this interval, $\partial^2 p/dt^2 = 0$ for alcohol, and therefore c_v is independent of the volume. For ether and carbon disulphide, on the other hand, $(\partial p/\partial t)_v = A + Bv$, in which A is a function of the temperature, and hence $\partial c_v/\partial_v = T\partial^2 p/J\partial t^2 = T\partial A/J\partial t$. Since the dependence of the specific heats, c_p, of these liquids on temperature has been investigated in this region by Battelli, it is possible to calculate c_v (for a mean volume, v). The following values for this factor are thus obtained:

	0°.	− 20°.	− 30°.	− 50°.	− 70°.	− 90°.
Ethyl alcohol............	—	—	0·406	0·386	0·370	0·358
Ethyl ether	—	0·397	—	0·386	0·376	0·362
Carbon disulphide ...	0·160	0·139	—	0·121	0·114	0·110

A bend such as would be expected from the Planck-Einstein formula is only observed in the case of ether when c_v is plotted against the temperature; the opposite bend observed with alcohol and carbon disulphide is attributed by the author to the existence of complex molecules in these liquids. H. W.

Thermodynamics of Chemical Equilibrium in Condensed Mixtures. H. Cassel (*Zeitsch. Physik*, 1920, **2**, 71—75).—This is a straightforward thermodynamic argument, apparently proving rigorously, from Planck's statement of the third law, that any difference between the specific heats of the mixture and of the components separately, or any thermal effect on mixing, or any curvature in the vapour pressure isotherms, is a sign of chemical action. The effect of volume changes or deviations of the vapour from the gas laws is neglected, however. Chemical Abstracts.

Thermodynamic Properties of the Ions of some Strong Electrolytes and of the Hydrogen Ion in Solutions of Tenth-Molal Hydrochloric Acid containing Univalent Salts. Herbert S. Harned (*J. Amer. Chem. Soc.*, 1920, **42**, 1808—1832).—Measurements of the electromotive forces of the cells

$$H_2|MCl(c) \text{ in } HCl\ (0{\cdot}1)|HgCl|Hg$$

at 18°, 25°, and 30°, containing potassium, sodium, and lithium chlorides, respectively, have been made. Assuming the complete dissociation of the above electrolytes, it is shown that the hypothesis of the individual ion activities as postulated by MacInnes (A., 1919, ii, 385) is true within narrow limits, and that at a given concentration of potassium chloride the potassium and chlorine ion activities are identical within narrow limits. The individual ion activity-coefficients of the hydrogen, potassium, sodium lithium, and chlorine ions from concentrations 0·1 to 3*M* have been calculated.

It is shown that the semi-empirical formula $\log F_a = \alpha c - \beta c^m$ where F_a is the activity-coefficient of the ion, c the concentration and α, β, and m are constants, will express F_a as a function of within experimental error from 0·01 to 3*M* concentration. A tabl

of the free energies and heat content decreases of the cell reaction $H_2 + 2HgCl = 2HCl(0{\cdot}1) + 2Hg$ in the presence of potassium, sodium, and lithium chlorides, respectively, has been compiled.

On the assumption that the ions have independent heat contents of transfer, and that at a given concentration of potassium chloride the potassium and chlorine ions possess identical heat contents of transfer from a solution of concentration c_1 to a solution of concentration c_2, it is possible to calculate the decrease of heat content of transfer of the hydrogen ion from solutions of MCl(c) in HCl (0·1) to HCl (0·1). The results are tabulated. This decrease is shown to be a function of the total ion activity of the solution, not of the activity of the hydrogen ion. J. R. P.

Equation of State Covering all States of Aggregation and the Law of Action of the Molecules. LEON SCHAMES (*Zeitsch. Physik*, 1920, **1**, 376—384).—The author derives values for some of the constants of his equation. CHEMICAL ABSTRACTS.

Melting-point Methods at High Temperatures. LEO I. DANA and PAUL D. FOOTE (*Trans. Faraday Soc.*, 1920, **15**, 186—217).—Detailed descriptions are given of the methods of determining the melting points of metals, inorganic salts, and silicates by means of thermocouples, resistance thermometers, and optical pyrometers, as well as special methods. The following melting points are recorded: tin, 231·9°; bismuth, 271°; cadmium, 320·9°; lead, 327·4°; zinc, 419·4°; antimony, 630·0°; aluminium, 658·7°; silver, 960·5°; gold, 1063·0°; copper, 1083·0°; nickel, 1452°; cobalt, 1480°; iron, 1530°; palladium, 1550°; chromium, 1615°; platinum, 1755°; silicon, 1420°; sodium molybdate, 687°; borax, 741°; sodium chloride, 801°; sodium sulphate, 884°; sodium metasilicate (Na_2SiO_3), 1088°; lithium metasilicate, 1202°; lithium orthosilicate (Li_4SiO_4), 1255°, and various silicates, aluminates, and refractory materials. J. R. P.

The Relation between Boiling Point in the Vacuum of the Cathode Light and Critical Temperature. P. WALDEN (*Zeitsch. anorg. Chem.*, 1920, **112**, 225—232).—Making use of the data given by Krafft (A., 1896, ii, 464; 1899, ii, 464) for a number of paraffins, fatty acids and their esters, and benzene homologues of high molecular weight, it is shown that the ratio of the absolute boiling point, T_{15} at 15 mm., to that, T_0, in the vacuum of the cathode rays, has a mean value of 1·2. The ratio between the boiling points at 15 mm. and 760 mm. is given by $T_{15}/T_{760} = 0{\cdot}765$. It follows that $T_{760}/T_0 = 1{\cdot}59$, which is identical with the mean experimental value for the higher paraffins. This value is practically identical with that found by van Laar for the ratio of the critical temperature to the boiling temperature at atmospheric pressure, $T_k/T_{760} = 1{\cdot}60$. Hence the critical temperature is 2·54 times the boiling temperature in the highest vacuum. In the case of the metals potassium, sodium, silver, and copper, the relation between T_{760} and T_0 is expressed by $T_{760} = 4{\cdot}55T_0/\log T_0$.

The above relation between critical temperature and boiling points is applied to calculate the critical temperature of metals. For those metals of which the boiling point in absolute vacuum is not known, this is calculated from the relation that $T_D/T_{vap.} = 1{\cdot}8$, where $T_{vap.}$ is the temperature at which vaporisation begins in the vacuum of the cathode rays. E. H. R.

Direct Measurement of the Thermal Molecular Velocity. OTTO STERN (*Zeitsch. Physik*, 1920, **2**, 49—56).—A silvered platinum wire is electrically heated in a high vacuum (0·0001 mm. Hg) until silver molecules leave it with a mean free path greater than the length of the containing vessel. Those of a certain direction are selected by passing two slits 0·2 mm. wide, and next strike a brass screen 10 cm. away, where they condense as a dark line. If the apparatus is rotated, the line is displaced by an amount from which the velocity of the molecules can be calculated. The speed of rotation was 1500 rev. per minute, and the displacement about 4 mm. The indirectly known value was confirmed to 15%, about the uncertainty due to imperfect knowledge of the temperature. The molecule of gaseous silver was shown to be monatomic. CHEMICAL ABSTRACTS.

Determination of Vapour Pressure. E. J. HARTUNG (*Trans. Faraday Soc.*, 1920, **15**, 150—159).—An improved tensimeter is described, which allows of the determination of vapour pressures with great accuracy. The vapour pressures at 0° of solutions of potassium chloride, potassium sulphate, and sulphuric acid were compared with that of a solution of potassium chloride saturated at 0°. J. R. P.

Vapour Pressure of Aqueous Solutions of Mannitol. J. C. W. FRAZER, B. F. LOVELACE, and T. H. ROGERS (*J. Amer. Chem. Soc.*, 1920, **42**, 1793—1808).—The vapour pressure lowerings of aqueous mannitol solutions have been determined over the range of solubility of the substance. The error due to dissolved air was eliminated. A mean deviation from Raoult's law of only 0·0006 mm. was found up to 0·8 molar concentration. By comparison with freezing-point lowerings, it is found that $\log_e p_0/p_1$ decreases with the temperature, or the heat of dilution has a small negative value for concentrations up to 0·5 molar. Comparisons with boiling-point determinations show that this changes to a positive value at higher concentrations. J. R. P.

Thermochemistry of Ionisation of Vapours of certain Compounds. PAUL D. FOOTE and F. L. MOHLER (*J. Washington Acad. Sci.*, 1920, **10**, 435—444).—If a material in the vapour state ionises by dissociation it is sometimes possible to calculate the ionisation potential from chemical and physical data. In the case of alkali-metal haloids, all the necessary data are known except the heat of sublimation. The heat of sublimation may be calculated

for haloids of metals of the second group from the vapour pressures. The ionisation potentials are computed for hydrogen chloride, bromide, iodide and sulphide, and the value for hydrogen chloride is found to be in agreement with the number determined by the authors. J. R. P.

Thermochemistry of Carbon Compounds. A. THIEL (*Ber.*, 1920, **53**, [*B*], 1378—1382).—A criticism of the work of Fajans (this vol., ii, 354) and von Steiger (this vol., ii, 355). The author considers that Fajans' calculations are to some extent based on fundamentally invalid assumptions. For example, the existence of monatomic carbon vapour is assumed into which carbon could only dissociate to the extent of about 50% at 10,000° according to calculations based on the theory itself. It is further assumed that the atoms in the crystal lattice of diamond are united to one another by the same valencies as in aliphatic compounds. In general, however, this can scarcely be the case, since it would then be impossible to explain the crystalline form of elements of lower valency; in all probability, only subsidiary valencies can be involved. H. W.

The Benzene [Formula] Problem. III. A. VON WEINBERG (*Ber.*, 1920, **53**, [*B*], 1353—1358).—As a result of recent experiments, Debye and Scherrer (A., 1917, ii. 437) have been led to the conclusion that carbon in the form of diamond is to be regarded as the prototype of aliphatic compounds, whilst graphite and amorphous carbon are the simplest stages in aromatic chemistry. The author does not regard the production of mellitic acid from graphite (and not from diamond) as valid evidence of aromatic nature, since it is not a primary product. Further, Debye and Scherrer have seen in the suppressed fourth valency of the carbon atoms in benzene an analogy to the mechanically suppressible fourth valency of the graphitic carbon atom, and point to the behaviour of the triarylmethyls as proof of the existence of such weakened fourth valencies; in reality, however, the valency is not weakened, as is evidenced by the behaviour of this class of substance towards oxygen, but only intermittently saturated in consequence of the induced vibrations of the central carbon atom. Von Steiger (this vol., ii, 355) has adduced evidence in favour of Debye and Scherrer's hypothesis by consideration of the heats of combustion of aromatic compounds. It is shown, however, that the energy involved in the isolation and combustion of a carbon atom in benzene is 5·3 Cal. greater than that involved in the case of an aliphatic hydrocarbon and 7 Cal. greater than that involved with graphite. It therefore appears that benzene rings cannot be present in graphite, and, more generally, that it represents a particular type of union. The kinetic formula for benzene leads to the hypothesis that the excess of energy (5·3 Cal.) for an aromatic in comparison with an aliphatic carbon atom is a consequence of its more rapid movement, and is the logical conclusion of the theory that the energy excess of

multiple bonds is kinetic in origin—a theory which is defended l examples against the criticisms of Fajans. H. W.

Heats of Combustion and Energy of Dissociation. A. von Weinberg (*Ber.*, 1920, **53**, [*B*], 1347—1353).—The prese communication contains a concise statement and justification of t views previously expressed in part by the author (this vol., ii, 1 and more recently criticised in some particulars by Fajans (tl vol., ii, 354). They may be expressed in the following manne (1) in saturated aliphatic hydrocarbons, the energy of dissociati of a C–C bond is equal to that of a C–H bond, that is, $Q_{CC}=Q_C$ (2) the absolute value of Q_{CH} is 7·5 Cal. greater than the energy *dissociation of a hydrogen molecule*; (3) *molecular cohesive for* have not to be overcome in the combustion of solid carbon, whi practically only requires the provision of the energy of four C vale cies for the carbon atom. The absolute value for diamond graphite is $2Q_{CC}+1·5$ Cal. (4) In the oxidation of carbon monoxi to carbon dioxide the energy of dissociation of the two so-call unsaturated valencies is equal to Q_{CC}.

(1) If it be admitted that the energy required for the separati of two similar or dissimilar atoms is evenly distributed between t atoms, the following expression is obtained for the energy of disn tion of a hydrocarbon, $C_nH_{2n+2}-[(n-1)Q_{CC}+2n+2/2\,.\,Q_{CH}]$ $[2n+2/2\,.\,Q_{CH}]$, in which the left bracket represents the ener required for the separation of n carbon atoms and the right brac that required for $2n+2$ hydrogen atoms. The contribution of t n carbon atoms towards the heat of combustion of the hydrocart is $nx=-[(n-1)Q_{CC}+(n+1)Q_{CH}]+nQ_{CO_2}-nQ_{O_2}$, where Q_{CO_2} a Q_{O_2} are the energies of dissociation of carbon dioxide and oxyg The summation law demands that this shall be true for any va of n, which can only be the case when $Q_{CC}=Q_{CH}$. (2) The values *the energy of dissociation* of a hydrogen molecule are calculated fr the recent experiments of Franck, Knipping, and Krüger. It is present impossible to elucidate the intramolecular process on wh the difference depends. (3) If 96 Cal. be adopted as the m probable value for the heat of combustion of solid amorph carbon, it appears that the latter behaves during combustion a gaseous saturated hydrocarbon. Solid carbon therefore occupie position different from that of all solid organic compounds, an appears *justifiable to conclude that liquid molecular carbon is in able of existence.* The *heat of combustion of diamond* has b determined with great accuracy to be 94·5 Cal., and this differe of 1·5 Cal. can only be explained on the supposition that the w of dissociation in diamond is correspondingly greater. (4) Thom has already endeavoured to calculate the absolute value for energy of dissociation of a carbon atom from solid carbon by c sideration of the oxidations of the element to carbon monoxide dioxide respectively, but the author holds this mode of reasonin be *incorrect, since it assumes the similarity of the C–O double b in carbon monoxide and the two C–O linkings in carbon diox*

Ie prefers to calculate Q_{CO} from the heats of combustion of a umber of aldehydes and ketones, and thus deduces the value 66·7 Cal. (the value may be slightly inaccurate on account of the experimental difficulties in working with the more volatile substances); the nean value of the heat of combustion of carbon monoxide as deternined by Berthelot and Thomsen is 67·4 Cal., a figure which agrees vith the former within the limits of experimental error. It follows, herefore, that the two so-called unsaturated valencies of carbon nonoxide are not free during combustion, but require as much nergy for their separation as does the carbonyl group of a ketone. t therefore seems probable that the four carbon valencies in carbon nonoxide are attached to the oxygen atom. H. W.

Heats of Combustion and Energy of Dissociation. II. A. VON WEINBERG (*Ber.*, 1920, **53**, [*B*], 1519—1528).—On the basis f the ideas developed in previous communications (this vol., ii, 14, nd preceding abstract), the author has calculated the energy necesary for the fission of the commoner atomic linkings in organic ompounds. In the following, the energy of dissociation is repreented by Q, and the index shows the linking concerned.

It is found that $Q_{CC} = Q_{CH} = Q_{C-O} = Q_{NH} = Q_{N-N}$, or that five of the ommonest linkings in organic compounds are almost equally stable t 18°. The elimination of the first oxygen atom from carbon ioxide requires an expenditure of energy equal to 126·7 Cal., whilst or the second oxygen atom 265·5 Cal. (approximately double that sed in the former case) are necessary. Q_{O-H} in ethyl alcohol and thylene glycol is calculated to be 96·8 and 98·7 Cal. respectively, whilst in water it is 99·2 Cal.; the difference lies within the limits f experimental error, but it is quite possible that the OH linking n alcohols is slightly less stable than in water. The values calcuated for $Q_{N\equiv N}$ and Q_{NC} are 266·4 Cal. and 233·1 Cal.; from this it ollows that the treble bond in the case of nitrogen, in contrast to hat of carbon, is exactly equivalent to three single bonds, and this xplains why substances containing the group C≡N or N≡N are ot possessed of the same lability and power of forming additive ompounds as are those containing the C⋮C group. Q_{NO} and Q_{NO_2} are 70·9 Cal. and 243·7 Cal. respectively. Q_{HCl} is calculated to 119·2 Cal., which is in good agreement with the value (119 Cal.) found y Born (this vol., ii, 156) by a totally different method, and thus trikingly confirming Born and Haber's prediction that the energy f dissociation, Q_{HCl}, is equal to the electronic affinity of the chlorine tom. Q_{CCl} is calculated to be 119·6 Cal., so that practically the ame expenditure of energy is necessary to separate the hydrogen ucleus from the electron, the hydrogen atom from the chlorine tom, and the latter from the carbon atom. Q_{Cl-O}, Q_{HBr}, Q_{CBr}, Q_{HI} nd Q_{CI} are 78·8, 76·3, 74·2, 59·4, and 54·5 Cal. respectively, so that romine and iodine are rather more firmly combined with hydrogen han with carbon. The equality of energy of dissociation and elecronic affinity is not found with bromine and iodine. The difference etween the energy of the corresponding linkings explains the differ-

nces in the reactivity of the alkyl haloids. Q_{S_2} is calculated to be 04·5 Cal., which is in good agreement with the value (103·6 Cal.) etermined experimentally by Budde. Q_{SO_2} and Q_{SO_3} are respecively 254·5 Cal. and 336·2 Cal.; Q_{CS} and Q_{H_2S} are 73·1 Cal. and 52·8 Cal. respectively (the latter value differing widely from that alculated by Born). For Q_{SCl} the values 76·4 Cal. and 71·2 Cal. are alculated from different compounds. H. W.

Heat of Oxidation of Glucinum. H. Copaux and 'h. Philips (*Compt. rend.*, 1920, **171**, 630—632).—From measureients of the heat of solution of glucinum and its oxide respectively ı hydrofluoric acid the author calculates the heat of oxidation of lucinum to be given by $Gl_{sol.} + O_{gas} = GlO_{sol.} + 151·5$ cal. W. G.

Physico-chemical Properties of Highly Concentrated ispersoidal Solutions of Noble Metals. N. I. Morosov *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 783).—The viscosity of a 7·7% silver solution at 19·5° is 1·1129 times that of water. The iscosity *decreases with increasing temperature, for example, the* me of flow for 17·7% silver solution at 19·5° is 49·7 sec. and at 1·5°, 37 sec. The study of dispersoidal solutions (viscosity, b. p., c.) of high concentrations undoubtedly will make possible a qualiitive correlation among the degree of dispersity, the concentration disperse phase and changes of properties of the disperse medium. Chemical Abstracts.

The Viscosity of Liquids. IV. Ideal Mixtures of the 'ypes Ether–Ether and Ester–Ester. James Kendall and lexander Holland Wright (*J. Amer. Chem. Soc.*, 1920, **42**, 776—1784. Compare A., 1914, ii, 109; 1917, ii, 524, 525).—The scosity curves for the following liquid systems have been deterined with the use of the Bingham viscosimeter: (1) ethyl etherhenetole; (2) ethyl ether–diphenyl ether; (3) phenetole–diphenyl her; (4) ethyl acetate–ethyl benzoate; (5) ethyl acetate–benzyl enzoate; (6) ethyl benzoate–benzyl benzoate. Although these mixıres are certainly very nearly ideal, yet the experimental data are ot reproducible satisfactorily by means of any known simple rmula. The logarithmic viscosity formula of Arrhenius gives ılues uniformly a little low; the cube root viscosity equation of endall and Monroe (*loc. cit.*) gives values uniformly a little high. ll other proposed formulæ are altogether out of agreement with ie figures of experiment. It is concluded that the experimental ork has advanced as far as possible, and that further progress must e preceded by fundamental advances in the theory of the subject. J. R. P.

The Influence of Temperature on the Surface Tension f Narcotics. Hans Winterstein [with (Frl.) Else Hirschberg] *Biochem. Zeitsch.*, 1919, **100**, 81—83).—The surface activity of enzamide, monacetin, salicylamide, and ethyl urethane increases 'ith a rise in temperature. S. S. Z.

The Influence of Hydrogen Sulphide on the Occlusion of Hydrogen by Palladium. II. EDWARD BRADFORD MAXTED (T., 1920, **117**, 1280—1288).

Adsorption from Solutions of Substances of Limited Solubility. M. POLÁNYI (*Zeitsch. Physik*, 1920, **2**, 111—116).—A mathematical paper. CHEMICAL ABSTRACTS.

Mechanism of the Surface Phenomena of Flotation. IRVING LANGMUIR (*Trans. Faraday Soc.*, 1920, **16**, 62—74).—The adsorption of organic substances with large molecules originates from certain atoms in the molecule. Wetting is due to the attraction between the material wetted and some active group in the liquid molecule. A study of cleaned and oiled glass surfaces showed that films of molecular thickness are sufficient to alter radically the surfaces of solids, both as regards the lubricating properties of these films and the contact angles made by water drops. The formation of froth depends on the presence of substances which can form a stable unimolecular film over the surface of each bubble. In order that a froth may readily form, it seems desirable to have present a soluble substance having a strong tendency to be adsorbed on the surface of the liquid. The presence of alkalis in flotation is to be avoided, probably because the hydroxyl ion tends to draw the carboxyl group of the fatty acid to itself rather than allow it to attach itself to the solid particles. The tendency of particles to attach themselves to bubbles of the froth is measured by the contact angle formed between the oily surface of the bubble and the contaminated surface of the solid. The selective action by which substances like galena are separated from quartz and calcite is dependent on the contact angle formed by the oiled surfaces rather than on any selective tendency for the oil to be taken up by some minerals more than by others J. R. P.

The Diffusion of Electrolytes into Jellies. III. The Relation of the Distance of Diffusion to the Diffusion Coefficient and its Dependence on the Concentration of the Indicators. OTTO FÜRTH, HANS BAUER, and HANSI PIESCH (*Biochem. Zeitsch.*, 1919, **100**, 29—64. See A., 1919, ii, 13; this vol., ii, 94).—The diffusion of various electrolytes in agar jellies was studied, and it was found that the laws of diffusion could also mostly be applied to diffusion into jellies. It was further found that the "invasion factor," that is, the relation of the distance of diffusion of the electrolyte in question to that of a sodium chloride solution of the same molecular concentration diffusing under the same conditions, was an approximate measure for the square root of the diffusion-coefficient. It is concluded from this that most electrolytes also penetrate jellies according to the mobility of their ions providing that chemical affinity and colloidal changes do not interfere. The

distance of diffusion is influenced by the concentration of th indicator in the jellies. S. S. Z.

The Effect of Asymmetry. A Study in Crystal Structure THOMAS VIPOND BARKER and MARY WINEARLS PORTER (T., 1920 **117**, 1303—1321).

The Electrochemical Behaviour of Mixed Crystals o Gold with Copper and Silver. G. TAMMANN (*Zeitsch. anorg Chem.*, 1920, **112**, 233—243).—In previous papers (A., 1919 ii, 398, 406) it has been shown that there is a limiting compositio for gold–copper and gold–silver alloys, such that, when the gol content exceeds this limit, the alloys are not attacked by differen chemical reagents. The limiting composition was correlated wit the probable distribution of the two kinds of atom on a fac centred cubic lattice in the crystalline structure of the alloy. Th electrochemical properties of these alloys have now been invest gated. When copper–gold alloys are used as anode in an electr lytic cell, with a copper cathode and copper sulphate or nitrat as electrolyte, the limiting composition is about 0·27 to 0·30 mo of gold; with a smaller proportion of gold than this, copper dissolved from the anode. With gold–silver alloys as anode, usin sulphuric or nitric acid as electrolyte, the limiting composition 0·35 to 0·40 mol. of gold. Similar limits were found when th decomposition potentials of such cells were measured. On th other hand, to obtain a persistent polarisation effect of 1·4 volts i the case of gold–copper and 0·73 volt for gold–silver, the propo tion of gold to silver or copper must not fall below 0·5 mol. Th normal limiting composition for weak oxidising agents, such hydrogen peroxide, in acid or alkaline solution is about 0·25 mo of gold; in the case of anodic oxygen, therefore, this normal lim is exceeded. The same is true of anodic sulphur, produced by th electrolysis of sodium sulphide, the limit in this case being mo than 0·50 mol. of gold.

Discussing these observations from the point of view of the spac lattice theory, the author points out that in an alloy containi 0·25 mol. of gold, that is, 1 atom of gold to 3 of copper, in t face-centred cubic lattice there will not be in any cube face pla any two copper atoms the distance of which from one anoth corresponds with the minimum translation in the lattice. T alloy would therefore be protected against attack by any age which needs two atoms of copper. If the agent can attack t copper, on the outer planes, but the gold atoms retain their po tions, then, if the agent cannot penetrate the structure, the all is still resistant.

The limiting composition for strong anodic polarisation of alloys, 0·5 mol. gold, is the same as the limiting composition gold–palladium alloys for hydrogen solubility. These facts may correlated with the presence in the structure of alloys containi 0·5 mol. of gold or less of cube edges or diagonals form exclusively of copper or silver or palladium atoms. E. H. R.

Relation between the Solubilities of Solutes and their Molecular Volumes. SHINKICHI HORIBA (*Trans. Faraday Soc.*, 1920, **15**, 178—185).—When a solute of molecular volume V is dissolved in a solvent of molecular volume v, the number of molecules of solvent which can surround one solute molecule is approximately $4/1{\cdot}1 \cdot (\sqrt[3]{V/v}+1)^2$, assuming that V is distinctly larger than v. If the logarithms of the solubilities are plotted against this expression, straight lines are obtained. J. R. P.

Mutual Action of Trimethylsulphanilic Acid and Strong Electrolytes. MASAO KATAYAMA and NOBUO YAMADA (*J. Tokyo Chem. Soc.*, 1920, **41**, 193—224).—It has been shown (*ibid.*, **36**, 745) that trimethylsulphanilic acid is not an electrolyte, but lowers the electrical conductivity of other electrolytes, due either to interference of ionic velocity of the electrolytes or to formation of complex salts. The authors failed to obtain the crystalline complex salts reported by Griess (A., 1880, 322), except when potassium salts were present. The complex salts prepared by Griess, therefore, must have either contained potassium salts or methylation must have been incomplete. From determinations of the transport number of hydrochloric acid containing the sulphonic acid, it is shown that there is no complex salt formation. Viscosity measurements of aqueous solutions of trimethylsulphanilic, hydrochloric, and acetic acids show that the effect is additive for acetic acid and the sulphonic acid, but is not so for hydrochloric acid and the sulphonic acid. The change of conductivity of both hydrochloric and acetic acids produced by the addition of the sulphonic acid is entirely due to the change of viscosity. The solubility and the change of volume produced when the sulphonic acid is added to water, hydrochloric acid, and acetic acid are also measured. The general conclusion is that hydrochloric acid increases the dissociation of trimethylsulphanilic acid, but the latter does not affect the dissociation of hydrochloric acid. CHEMICAL ABSTRACTS.

Reversible and Irreversible Dispersoidal Parasitism. P. P. VON WEIMARN, N. I. MOROSOV, and V. J. ANOSSOV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 782).—An investigation on the conditions of formation of dry and solid preparations of silver, which are reversibly soluble, leads to the following conclusions: Dispersoidal parasitism is reversible in the limits of ordinary temperature (20—25°) only when the substance which originates it is soluble at these temperatures. Examples: silver + gum, silver + dextrin. Dispersoidal parasitism is irreversible in the limits of the ordinary temperature if the substance which originates it is insoluble at these temperatures. Examples: silver + agar, silver + gelatin. Gelatin and agar are therefore stabilisers only for liquid preparations of dispersoidal silver, and the dried preparations do not dissolve in water at 20—25°. A method has been developed for obtaining liquid solutions of silver of very high dispersity; concentrations of 15% and more are easily obtainable in about one hour. CHEMICAL ABSTRACTS.

Method of obtaining Dry Precipitates of any Insoluble Substances, which pass into Dispersoidal-dissolved State Commencing only from some Fixed Temperatures. P. P. von WEIMARN, N. I. MOROSOV, and V. J. ANOSSOV (*J. Russ. Phys Chem. Soc.*, 1916, **48**, 197).—Dispersoidal parasitism is characterised by the fact that any insoluble substance (for example, silver sulphur, barium sulphate, etc.) receives nearly the same properties of "solubility" as a substance at the expense of which it parasites Therefore, by mixing together any insoluble precipitate of high dispersity with various substances which are parasitised and which are sufficiently soluble, for example, successively at 10°, 20°, 30° 40°, etc., there is obtained a succession of dry preparations of the insoluble substance. These preparations are "soluble" also successively in the vicinity of temperatures enumerated above Many organic substances (solutoids, for example, gelatin), on heating of their solutions for a long time, give products soluble at still lower temperatures than the original substance. These temperatures are lower the longer the solution is heated. These products are especially convenient for realisation of the method here described. For example, a dry precipitate of dispersoidal silver (63% of Ag) which is prepared with gelatin, previously boiled for seven hours, practically "does not dissolve" in water at about 20°, but it "dissolves" excellently at about 35°, giving very stable silver "solutions" of high dispersity. CHEMICAL ABSTRACTS.

Coagulation of Agar-agar Hydrosol. KEIZO IWAS (*J. Tokyo Chem. Soc.*, 1920, **41**, 468—479).—The effects of temperature and of salts on the velocity of coagulation were studied Agar-agar was washed with dilute acetic acid, water, aqueous ammonia, and water, dissolved by heat, and then filtered. The precipitate produced by alcohol, and dried with alcohol and ether was a white powder. A known concentration of agar-agar was prepared by dissolving this powder and heating under a reflux condenser. The hydrosol thus obtained was transferred to test tubes and kept in a bath 20° higher than the temperature under which experiments were to be conducted. The end-point of the coagulation was taken at the time when the agar not only would not flow, but also its surface meniscus could not be disturbed on inverting the test-tube. The general conclusions are: The more concentrated the hydrosol, the greater is the speed of coagulation The effect of the salts on coagulation time is greater when the hydrosol is the more concentrated. Series of ionic effect are $K>Na, SO_4>CH_3\cdot COO>C_6H_4O_6>Cl>Br>NO_3>I$. Although the temperature effect on the speed of coagulation is very great, the order of this series of the salt effect at different temperatures does not change. The heating of the sol prolongs the time of coagulation, finally rendering it non-coagulable. CHEMICAL ABSTRACTS.

Sedimentation. PETER RONA and PAUL GYÖRGY (*Biochem Zeitsch.*, 1920, **105**, 133—140).—According to Bodländer (*Jahrb. Min.*, 1893, **2**, 147), small proportions of electrolyte

soluble in water cause rapid clarification of kaolin suspensions, whereas soluble non-electrolytes, even in large amounts, are ineffective in this respect (compare Kruyt and van Duin, A., 1914, ii, 182; Freundlich and Rona, A., 1917, ii, 365; Rona and Michaelis, A., 1919, ii, 269). The authors have now made further experiments with methyl, ethyl, *iso*propyl, amyl, heptyl, *n*- and *sec.*-octyl, and decyl alcohols, methyl-, ethyl-, propyl-, *iso*butyl-, and phenyl-urethanes, diphenylthiocarbamide, chloroform, tributyrin, camphor, and thymol, and find that nearly all of these non-electrolytes increase the velocity of sedimentation of kaolin. In homologous series, this acceleration increases in magnitude with the length of the chain, and only with compounds virtually insoluble in water is no effect detectable.

The increases in the viscosity of water produced by these compounds are at most very small, and the authors assume that the non-electrolytes produce a sensibilisation of the suspended particles towards the electrolytes always present, and thus increase the velocity of sedimentation of the kaolin particles. This view is supported by the observation that the velocity of sedimentation of charcoal is not influenced by non-electrolytes. T. H. P.

Structure of Precipitates. SVEN ODÉN (*Svensk. Kem. Tidskr.* 1920, **32**, 90—98; from *Chem. Zentr.*, 1920, iii, 326—327. Compare this vol., ii, 600).—The author has endeavoured to develop a theory concerning disaggregation and aggregation with increasing electrolyte content, but the subject is difficult, on account of the limited knowledge regarding the electrical double layer. Freundler's absorption formula may be adopted, and the assumption may be made that for each type of ion a special adsorption isotherm of the form $y=\beta c^{a}$ exists in which the coefficient is greater for one variety of ion and the exponent greater for the other. The derived relationships are expressed by graphs. The author considers that the so-called peptisation of a precipitate consists exclusively in the adsorption of ions, with discharge of the primary particles and subsequent scattering of the aggregates. The influence of concentration, temperature, and rate of admixture of the reacting solutions on the size of the primary particles has been accurately investigated. The effect of concentration on the structure of precipitated barium sulphate has been examined with solutions of barium thiocyanate and ammonium sulphate. If the concentration of the supersaturated barium sulphate solution at the moment when primary particles separate be denoted by M it appears that, with diminishing concentration of the reacting solutions, the primary particles are of sufficient size to remain stable when $M=0{\cdot}25$. The distribution curves for the magnitude of the particles are given. If one solution is added drop by drop to the other, the barium sulphate primarily formed separates at a considerably lower value of M, and consequently in correspondingly larger particles than if the total quantity of barium sulphate is simultaneously produced. The influence of rate of addition on the primary structure is quantitatively examined with the help of

solutions of barium nitrate and ammonium sulphate, and the results are given in a series of graphs. Finally, the effect of temperature is studied, and the well-known phenomenon that precipitated barium sulphate becomes coarser with increasing temperature is quantitatively examined. H. W.

Copper Ferrocyanide. E. J. HARTUNG (*Trans. Faraday Soc.*, 1920, **15**, 160—177).—Preliminary experiments on the equilibrium between moist copper ferrocyanide and aqueous vapour, and on the adsorption of potassium chloride and potassium sulphate from solutions by copper ferrocyanide, are described. The function of copper ferrocyanide in semi-permeable membranes is discussed.
J. R. P.

Equation for the Chemical Equilibrium of Homogeneous Mixtures. ALFRED W. PORTER (*Trans. Faraday Soc.*, 1920, **15**, 75—82).—A mathematical paper in which the conditions for the equilibrium of a homogeneous mixture at constant temperature, and the effect of pressure on the equilibrium constant, are deduced by rigorous methods. J. R. P.

Self-ignition of Ethyl Ether–Air Mixtures. J. A. McCLELLAND and H. V. GILL (*Sci. Proc. Roy. Dublin Soc.*, 1920, [N.S.], **16**, 109—119).—Ignition occurs when a mixture of ethyl ether vapour and air is allowed to rush into a partly exhausted tube. Measurements of the temperature in the tube showed that the rise of temperature produced reached the ignition point of the mixture. The rise of temperature is attributed to the conversion into heat of the translational energy of the gas rushing into the tube. The length of the explosion tube affects the results. J. R. P.

Theory of Velocity of Reaction. M. POLÁNYI (*Zeitsch. Physik*, 1920, **2**, 90—110. Compare this vol., ii, 238).—The non-mechanical nature of chemical processes, considered in conjunction with the quantum hypothesis, leads to the conclusion that chemical decomposition is influenced by atomic vibrations. It is assumed that these vibrations are irregular. Formulæ have been deduced for the reaction velocity of different types of chemical processes. CHEMICAL ABSTRACTS.

Velocity of Unimolecular Reactions. ERIC K. RIDEAL (*Phil. Mag.*, 1920, [vi], **40**, 461—465).—A theoretical paper in which unimolecular reactions are considered from the point of view of the radiation hypothesis. It is shown that the reaction velocity of a unimolecular reaction is given by the expression $dn/dt = \nu \cdot e^{-h\nu/kT}$, where ν, the activating radiation frequency, is identical with the time of molecular relaxation. On the basis of the radiation theory, light would appear to be corpuscular, the size

of a quantum being equal to a wave-length of light. If its energy be due to an electrostatic charge, E, then $E^2 = 2hc$. J. F. S.

The Propagation of Flame in Mixtures of Methane and Air. II. Vertical Propagation. III. Propagation in Currents of the Mixtures. WALTER MASON and RICHARD VERNON WHEELER (T., 1920, **117**, 1227—1240).

Kinetics of the Reaction of Nitrous Acid, particularly towards Halogen Oxyacids. ALBIN KURTENACKER (*Monatsh.*, 1920, **41**, 91—113. Compare A., 1914, ii, 552; 1915, ii, 537, 622). —The action of sodium nitrite in aqueous solution towards potassium chlorate, dichromate, and permanganate in the presence of potassium hydrogen sulphate has been kinetically investigated. With the first two oxidising agents, the solutions of sodium nitrite and potassium hydrogen sulphate are mixed at 20°, and, after a period of about fifteen minutes, during which the solution acquires a steady condition, the agent is added. Aliquot portions of the mixture are removed at definite intervals and almost neutralised by alkali; the nitrous acid is destroyed by protracted ebullition with ammonium sulphate, and the unchanged oxidising agent is estimated by the addition of a measured volume of ferrous sulphate solution, followed by titration of the excess of the latter with $N/10$-permanganate solution. In the case of potassium permanganate, reaction proceeds very rapidly, even in dilute solution, and the measurements are effected by noting the time necessary for the decolorisation of a known quantity of permanganate by potassium nitrite in the presence of acetic acid.

The chlorate–nitrite reaction can be expressed by the formula $dx/dt = [K_1 + K_2S](ClO_3')(HNO_2)$, where K_1 is the velocity-coefficient of the uncatalysed action, K_2 the acceleration-coefficient of the acid, and S the concentration of the latter, whilst with dichromate the expression becomes

$$dx/dt = [K_1 + K_2(S)^2](H_2Cr_2O_7)(HNO_2).$$

In all probability it is the undissociated nitrous acid, and not the nitrite ion, which takes part in the change. Similarly, the catalytically accelerating action of the added acid

$$(KHSO_4, CH_3{\cdot}CO_2H)$$

is probably to be attributed to the undissociated molecules (or HSO_4' ions), and not to the hydrogen ions. The independence of the rate of reaction of the concentration of the nitrite, which is a feature of the bromate reaction, is not observed in any of the new cases under investigation. Very marked differences are found in the mechanism of the action of chloric, bromic, and iodic acids respectively; the greatest abnormality is observed with bromic acid, which, in contrast with its position in the natural series, acts much more rapidly than either chloric or iodic acid. Further experiments with other oxidising agents will be necessary to elucidate the reasons of this divergent behaviour. Permanganate reacts

much more rapidly with nitrous acid than does any other oxidising agent. H. W.

Comparative Rate of Hydrolysis of the Fatty Esters of Different Alcohols. H. HEINRICH FRANCK (*Seifenfabr.*, 1920, **40**, 293—294; from *Chem. Zentr.*, 1920, iii, 337).—In order to investigate the relationship between resorption and rate of hydrolysis of fatty esters, the author has determined the latter factor for linseed oil and for the ethyl and ethylene esters of the fatty acids of this oil. The substances were dissolved in light petroleum and treated with alcoholic-potassium hydroxide solution at 34° or 4°, the free acid being periodically tested. Differences in the rates of hydrolysis were not great, the glyceryl ester being most rapidly, and the ethyl ester least readily, affected. With esters of the polyhydroxy-alcohols, the curves showing the rate of hydrolysis indicate a primary rise followed by a distinct minimum, which is apparently due to temporary formation of the ethyl ester. Enzymic fission by "steapsin Grübler" was also investigated, and the curves again show a minimum after an initial maximum. In agreement with other experiments, the order glyceryl, ethyl, ethylene ester is established. H. W.

The Hydrolysis of Platinum Salts. I. Potassium Platinichloride. EBEN HENRY ARCHIBALD (T., 1920, **117**, 1104—1120).

Significance of Neutral Salts as Catalysts in Chemical Reactions. OSKAR BAUDISCH (*Biochem. Zeitsch.*, 1920, **106**, 134—138).—The author confirms the observation of Wurster (A., 1889, 1242) that hydrogen peroxide and a solution of *a*-naphthylamine in dilute acetic acid react, with formation of a colouring matter, in presence of sodium chloride. It is found that the reaction takes place instantaneously in presence of lithium chloride, almost as quickly with magnesium, calcium, or aluminium chloride, and only after the lapse of several minutes with sodium, ammonium, or potassium chloride. The sulphates and nitrates corresponding with these chlorides are inactive in this respect, as also are potassium sodium tartrate and potassium citrate and acetate. In place of *a*-naphthylamine, any other readily oxidisable aromatic amine may be employed, but *β*-naphthylamine does not respond to the reaction. The pronounced effect produced by lithium chloride is doubtless due to the stronger secondary valencies of the lithium in comparison with those of sodium and potassium, the aromatic amine to be oxidised first undergoing loose union with the central lithium atom. The oxidation of aniline salts or benzidine by means of sodium ammonioprusside in presence of atmospheric oxygen or hydrogen peroxide does not seem to differ fundamentally from the oxidation of aniline acetate by means of hydrogen peroxide in presence of lithium chloride. The well-known oxidation of ammonia to nitrous acid by the agency

ɔpper hydroxide and atmospheric oxygen is probably of the same ıaracter; just as in the oxidation of ammonia by hydrogen per-ɛide in presence of sodium chloride, the ammonia first enters into ›-ordinative union with the central metallic atom, oxidation to ıtrous acid by the activated oxygen then occurring readily.

T. H. P.

Studies in Catalysis. XIV. The Mechanism of the ıversion of Sucrose. CATHERINE MARGARET JONES and 'ILLIAM CUDMORE McCULLAGH LEWIS (*T.*, *1920*, **117**, '20—1133).

Catalysis in the Hydrolysis of Esters by Infra-red adiation. ERIC KEIGHTLEY RIDEAL and JAMES ARTHUR HAWKINS :., 1920, **117**, 1288—1296).

Origin of the Elements. [J. H. VINCENT (*Proc. Physical ɪc. London*, 1920, **32**, 271—290).—A theoretical paper in which ʏpotheses in connexion with the origin of the elements are put ɾward. The atomic weights are regarded as the weighted mean ılues of the atomic weights of the isotopes of the elements, but is assumed that, as a rule, the atomic weight of the ordinarily ːcurring element is near to that of some one isotope. Figures and .bles are drawn up showing how this accounts for the accepted ılues of a large number of atomic weights, if it is also assumed ıat the weights and positions in the periodic table of any isotope 'e conditioned by laws similar to those holding in the recognised .dioactive families. The elements are all supposed to be derived om parent elements by processes known to occur in actively diating families, but their radioactivity is not, in general, detect-ɔle by the usual means, owing to the velocity of expulsion of the ırticles being low. The possibility of the reversibility of radio-'tive processes is considered, and regarded as probable in certain ses. Difficulties in connexion with the views expressed are con-lered. The hypothesis is used to explain the laws (so-called) of ɩe atomic weights of elements of small atomic weight, and the .ape of the curve obtained when the atomic weights are plotted ;ainst Moseley's numbers.

J. F. S.

Dimensions of Atoms. A. O. RANKINE (*Phil. Mag.*, 1920, i], **40**, 516—519).—A theoretical paper in which the atomic ameter of argon, neon, krypton, xenon, chlorine, bromine, iodine, ːygen, and nitrogen, as found by Bragg from crystal measure-ents (this vol., ii, 537), are compared with the values found by .e author from viscosity measurements (A., 1910, ii, 188, 409, !9; 1912, ii, 332). It is shown that the values obtained by the tter method are somewhat larger than those obtained by the rmer, but that the increment in the diameter, in passing from ıe member of a group to the next, is generally about the same the two sets of values.

J. F. S.

Constitution and Structure of the Chemical Element HAWKSWORTH COLLINS (*Chem. News*, 1920, **121**, 157—159).—*A continuation of a former paper* (this vol., ii, 26), in which element heavier than manganese are included. The sodium atom is sup posed to enter into the constitution of heavier atoms, and th addition of a mass of 23 always corresponds with the gain or los of one electron. It is shown by calculation that the results canno be due to chance. J. R. P.

Five Main Principles in the Constitution and Structur of the Chemical Elements. HAWKSWORTH COLLINS (*Chem News*, 1920, **121**, 182—185).—(1) Single chemical valencie emanate from elements or portions of elements the masses of whic are 1, 3, 7, 23, and 39. (2) The non-metallic nature of an elemen is always due to a pair or pairs of electropositive forces, each pai emanating from a portion of the element, of which the mass is 4 taking the mass of an atom of hydrogen as unit. (3) Monadi Na (23) takes a prominent part in the formation of all element of greater mass than itself. (4) In the simpler elements, H (1 forms the connecting link between the other portions, 3, 7, 2 and 39. In the formation of the heavier elements, masses of 2 sometimes unite by forces which are not chemically evident with out any intervening unit mass. (5) Each of the heavier elements formed by the union of simpler elements (which are indicated i each case by mineralogical and chemical facts combined). J. R. P.

Representation of the Periodic System of the Element by a Three-dimensional Spiral. GEORG SCHALTENBRAN (*Zeitsch. anorg. Chem.*, 1920, **112**, 221—224).—The elements ar arranged in order of atomic weight on an eccentric spiral. Th spiral has turns of four kinds of increasing circumference. Th first, smallest turn carries the elements hydrogen and helium, an is followed by a larger turn corresponding with the first sho period of the periodic table. The short turn is then repeate carrying neon and fluorine, and in successive similar short turn appear an inactive element and a halogen. The long periods the table are represented by correspondingly large turns of th spiral, and the largest turn of all carries the rare earth element Elements belonging to the same group in the periodic table lie a vertical plane passing through the axis of the spiral. E. H. R.

The Melting Point, Atomic Volume, and the Atomi Number of the Elements, and the Restoring Force of th Atoms. SUMINOSUKE ONO (*Proc. Phys. Math. Soc. Japan*, 191 [3], **1**, 251—260).—By means of Lindemann's formula, approx mate but simple quantitative relations between the atom numbers and melting points, etc., are deduced, and are given the form of charts. CHEMICAL ABSTRACTS.

Atomic Forces. W. KOSSEL (*Zeitsch. Physik*, 1920, **1**, 395—415. Compare A., 1916, ii, 243).—A discussion of the general nature of chemical bonding. The two main classes are: (1) heteropolar, where the forces are electrostatic and between different kinds of atoms, depending on the valence electrons, and (2) homopolar, generally between the same kind of atoms or molecules. In (2) the bonding is generally due to the holding of outer electrons in common, and their periodic properties can be predicted by assuming that atoms tend to take up electrons to form the stable configurations of the noble gases. The bonds considered may be those between atoms or between molecules, the two being sometimes indistinguishable, as in the case of the sodium chloride lattice. The two classes may be combined, as in the case of silicon tetrachloride, where the submolecular forces belong to (1) and the intermolecular to (2). The haloids of (1) (alkali and alkaline earth) are characterised by decrease of stability (m. p.) with increasing molecular weight of the halogen, whilst those of (2) show the reverse. Many other periodic characteristics are discussed.

CHEMICAL ABSTRACTS.

Percentage Curves of Carbon Compounds. ALEXANDER LANKE (*Oesterr. Chem. Zeit.*, 1920, **23**, 98—101, 106—108).—A mathematical paper in which the numbers of carbon atoms in organic compounds are represented as abscissæ and the percentage of carbon as ordinates. The resulting curve is called a percentage curve. For all hydrocarbons except C_nH_{2n}, these curves are parabolas. For hydrocarbons, C_nH_{2n}, they are straight lines. The influence of substitution is considered. J. R. P.

The Theory of Molecular Compounds. PAUL PFEIFFER (*Zeitsch. anorg. Chem.*, 1920, **112**, 81—96).—In certain respects, Werner's co-ordination formulæ, as applied, for example, to the cobaltammines, are unsatisfactory. It is difficult to understand, for instance, in the hexammine chloride, $Co[(NH_3)_6]Cl_3$, how the field of affinity between the cobalt and chlorine atoms can extend over the field of affinity of the ammonia molecules, especially in view of the strong affinity between hydrogen and chlorine. The variation of the total valency of cobalt between 6 and 9 in the cobaltammine group is also difficult to understand. The author applies the principle of "affinity adjustment of the valencies" to overcome the difficulties. In molecular compounds, such as the cobaltammines, the cobalt atom is assumed to have a fixed co-ordinative valence of 6, corresponding with the number of groups in the inner sphere of Werner's formulæ. The ionisable radicles or atoms in the outer sphere are then considered to be combined with the complex radicle as a whole, not attached definitely to the cobalt atom or to any of its associated molecules. The same idea is applied to the complex platinum salts.

Complex organic molecular compounds, such as those formed between aromatic hydrocarbons and di- or tri-nitrobenzene, or between hydrocarbons and quinones, are also considered. There

is, in general, no connexion, for example, between the number nitro-groups in a compound and the number of aromatic nu with which it will combine. In such cases, the compounds formed by the saturation of polyatomic valence fields on both sid In some cases it is conceivable that a polyatomic valence field n be saturated by combination with a monatomic field, for instan when a quinone, with two unsaturated carbonyl oxygen ato combines with two benzenoid nuclei. In other classes of c pounds, for instance, the compounds between tin tetrachloride a two molecules of a ketone, a compound of the co-ordinative t may be formed, the tin in this case having a co-ordinative vale of 6, thus:

$$\underset{\text{VI}}{\mathrm{Sn}}\mathrm{Cl_4}\begin{matrix}\cdot \mathrm{O{:}CR_2} \\ \cdot \mathrm{O{:}CR_2}\end{matrix}$$

In the crystal structure of simple organic molecular compou of the type *AB*, it is probable that each constituent acts as co-ordination centre, so that complexes of the type AB_6 and *B* interpenetrate, as they do in a rock-salt crystal. This wo explain the predominance of the simplest type of such molecu compounds. E. H. R.

Back-pressure Valves for Water Filter Pumps. E. Pin (*Chem. Zeit.*, 1920, **44**, 671).—To prevent water passing int flask under exhaustion from a water-pump, owing to an alterat in the water pressure, a simple valve is inserted by means of rub tubing between the pump and the flask, manometer, etc. T consists of a short glass tube constricted at each end to a sm opening. Within this is a short glass rod, one end of which fitted into a piece of pressure rubber tubing, whilst the other e is somewhat flattened, and also capped with rubber, a narr space for the passage of air being left between the rubber tubi and the inner wall of the glass tube. The rod is thus movab and so long as the pump is working normally is forced against constriction nearest the pump, still leaving a passage for the but should any water enter the tube from the pump, the rod immediately driven back against the other constriction, the op ing in which it seals, so that neither water nor air can enter flask. C. A. M

Laboratory Apparatus for Delivering Small Quantities Gas for Admixture with Other Gases in Constant P portion. Robert Mezger (*Chem. Zeit.*, 1920, **44**, 658—659).— the delivery of a constant supply of a gas (for example, ammon in definite proportion to another gas, the ammonia is generated heating ammonium chloride and moistened lime in a rou bottomed flask supported in a basin of mercury. Through stopper of the flask passes one arm of a T-tube, whilst anot branch of this is connected with a mercury thermo-regulator c trolling the supply of gas to a Bunsen burner beneath the bas There is also a pilot flame, with an independent gas supply, adjo

ng the Bunsen tube. The other outer limb of the T-piece conducts the ammonia into a capillary tube, which is connected with a wider tube, bending first laterally and then upwards to join a second T-piece. One arm of this communicates with a measured supply of a gas or of air, whilst the other is fitted into a reaction tube packed with glass wool. The pressure is shown on a mercury manometer between the ammonia flask and capillary tube. After removal of air from the apparatus by means of ammonia, the flask is connected with the capillary, and the tap communicating with the thermo-regulator opened. As soon as the pressure rises sufficiently, the gas is cut off from the Bunsen burner, and only the minute flame is left, until the pressure falls again, the gas is re-lighted from the pilot flame, and ammonia again evolved, and so on continuously. The regulation of the ammonia supply is effected by means of the capillary tube. For a definite capillary and kind of gas, the consumption of the gas (in this case ammonia) in c.c. per second (v) is found by means of the following modification of Poiseuille's formula, $v=K.H$, where H represents the difference of pressure and K a constant depending on the capillary and the gas used. In the case of ammonia, it may be found by varying the difference in pressure and estimating each time the corresponding amounts of ammonia by absorption in standard sulphuric acid. By plotting the results for v in a co-ordinate system, the volume of gas corresponding with any required pressure may be read directly. C. A. M.

Lecture Demonstration of the Instantaneous Combination of Bromine with Hydrogen and of the Chlorination of Magnesium in the Form of Magnesium Wool. OTTO OHMANN (*Ber.*, 1920, **53**, [*B*], 1429—1430).—Bromine (four to six drops) is placed in a litre gas cylinder, which is shaken until complete evaporation has occurred. The cylinder is brought mouth to mouth with a similar jar filled with hydrogen, and, when diffusion has taken place, the mixture is ignited with a red-hot wire. Combination occurs instantaneously with a perfectly harmless explosion, which is due to the union of excess of hydrogen with residual atmospheric oxygen. If more bromine is used, and, in consequence, less air is left, union occurs at once and without explosion, but with production of a peculiar blue flame.

A pad of magnesium wool, lightly sprinkled with finely divided antimony, is fixed to an iron wire and plunged into a jar of chlorine. The spontaneous ignition of the antimony causes the magnesium to burst into vigorous combustion, yielding a product which covers the whole of the inside of the vessel in the form of a snow-white, voluminous powder. H. W.

Lecture Experiments. Critical Examination of well-known Experiments with Metallic Sulphides. R. WINDERLICH (*Zeitsch. physikal. Chem. Unterr.*, 1920, **33**, 100—103; from *Chem. Zentr.*, 1920, iii, 429).—Strictly speaking, the union of iron and sulphur cannot be used as an illustration of the

of constant composition or as an obvious illustration the differences between mixtures and compounds. A mix- e is preferably demonstrated by finely powdered quartz l salt; the mixture of flowers of sulphur and iron filings ords a simple example of a chemical process which, started at e point, proceeds through the whole mass by reason of the great at of reaction. The statement, common in many elementary xt-books, that hydrogen sulphide does not give a precipitate with lutions of ferrous salts is only true when the latter contain ineral acid. The proportions of sulphur and oxide of iron escribed for demonstration are not in accordance with the nounts calculated from the equation $2Fe_2O_3 + 7S \longrightarrow 4FeS + 3SO_2$, artly because an excess of sulphur must be taken to counterbalance hat lost by volatilisation, and partly to inhibit the formation of ilphate, which occurs in the presence of a deficiency of sulphur.

H. W.

Inorganic Chemistry.

The Preparation of Chlorine from Hydrochloric Acid or Chlorides by means of Nitric Acid. JULIUS BAUMANN (*Chem. Zeit.*, 1920, **44**, 677).—The chlorine in chlorides or hydrochloric acid can be converted quantitatively into free chlorine by the action of nitric acid of about 52·0% strength, and the whole of the nitric acid recovered unchanged when the proper working conditions are observed. The points to be observed are to charge the chloride, for example, sodium chloride, slowly into the boiling acid and to use a long dephlegmator, whilst a current of air passes into the reacting gases. The following gas reactions involved, namely, $NOCl + HNO_3 = N_2O_4 + HCl$, $2HCl + N_2O_4 = N_2O_3 + Cl_2 + H_2O$, and $N_2O_3 + O_2 + H_2O = 2HNO_3$, then have time to complete themselves, and chlorine passes over practically free from hydrochloric acid whilst the whole of the nitric acid flows back into the reaction vessel.

E. H. R.

Electrolytic Formation of Perchlorate from Chlorate. J GUILFOYLE WILLIAMS (*Trans. Faraday Soc.*, 1920, **15**, 134—137) —The production of perchlorate by electrolysis is considerabl improved if a higher temperature of the liquid is maintained, an the frequent addition of acid improves the efficiency still mor During electrolysis, chloride is produced, and there is a equilibrium value for each temperature.

J. R. P.

The Relationship of Iodine and Bromine to Oxyge G. GRUBER (*Zeitsch. physikal. Chem. Unterr.*, 1920, **33**, 107—10 from *Chem. Zentr.*, 1920, iii, 434).—Direct replacement of brom by iodine occurs when the latter acts on an aqueous solution

potassium bromate; a similar action is not observed with bromine and potassium chlorate. Iodine attacks potassium chlorate in a less simple manner than potassium bromate, the change passing through the phases indicated by the equations $2KClO_3 + 2I + H_2O = KHI_2O_6 + KCl + HClO$, $KHI_2O_6 + KCl + HClO = 2KIO_3 + H_2O + Cl_2$, and $3HClO = HClO_3 + 2HCl$. H. W.

Preparation of Thionyl Fluoride and Attempts to Prepare Carbonyl Fluoride. WILHELM STEINKOPF and JULIUS HEROLD (*J. pr. Chem.*, 1920, [ii], **101**, 79—81).—A modified method of preparing thionyl fluoride by the interaction of thionyl chloride and arsenic fluoride is described. A brass flask is provided with an upright condenser, which is connected by a bent tube to a second condenser cooled with ice-water, which leads to a leaden vessel cooled to $-50°$ to $-60°$. The flask is initially cooled by ice and contains the arsenic fluoride, to which the calculated quantity of thionyl chloride is gradually added through a dropping funnel; the latter is then removed, and the flask is slowly warmed to about 80°, when the thionyl fluoride distils into the leaden receiver, whilst arsenic fluoride and chloride and thionyl chloride are held back by the reflux condenser. The attempts to prepare carbonyl fluoride were not completely successful, probably because platinum apparatus was not available. The best results were obtained by heating a mixture of arsenic fluoride and carbonyl chloride in a lead-lined iron or brass vessel provided with an upright condenser; the process is carried out during several hours on the water-bath with intermittent condensation of the products. Impure *carbonyl fluoride* was thus obtained as a readily decomposable substance, which solidified in liquid air and had b. p. about $-160°$ to $-150°$. H. W.

The Decomposition of Persulphuric Acid. HERMAN PALME (*Zeitsch. anorg. Chem.*, 1920, **112**, 97—130).—The rate of decomposition of potassium persulphate in solutions of 5·0, 7·53, and $10N$-sulphuric acid at 50° has been studied. Since the reaction proceeds through the stages, persulphuric acid ⟶ Caro's acid ⟶ hydrogen peroxide, it was necessary to develop a method for estimating these substances when all present in the same solution. Advantage was taken of the fact that Caro's acid reacts immediately with potassium iodide, whilst hydrogen peroxide reacts much more slowly, and persulphuric acid slowest of all. A sample of the solution is mixed with potassium iodide and titrated rapidly with sodium thiosulphate, the time taken being noted, so that a correction can be applied for the small quantity of iodine liberated by the hydrogen peroxide and persulphuric acid. The quantity of Caro's acid is thus found. A second sample is then treated with potassium iodide and titrated with sodium sulphite, which reduces hydrogen peroxide. This second titration gives the sum of Caro's acid and hydrogen peroxide. Finally, the persulphuric acid is estimated in a third sample by adding the calculated quantity of

sodium sulphite to reduce the other two compounds, and estimating the persulphuric acid by the ferrous sulphate–permanganate method. The dilution for the titrations corresponded with 2·0 grams of potassium persulphate per litre, of which 200 c.c were titrated at a time.

The experiments showed that, within the limits of error, the two reactions, $H_2S_2O_8 + H_2O \xrightarrow{k_1} H_2SO_5 + H_2SO_4$ and $H_2SO_5 + H_2O \xrightarrow{k_2} H_2O_2 + H_2SO_4$, can be regarded as unimolecular and irreversible. With increasing concentration of sulphuric acid, both velocity-constants increased at a greater rate than the acid concentration, but the ratio k_1/k_2 remained constant, 39·8. No relation between hydrogen-ion concentration and velocity of reaction could be discovered, and the conclusion of Levi and Migliorini (A., 1907 ii, 81) that undissociated persulphuric acid, the presence of which would be favoured by increasing hydrogen-ion concentration, is less stable than its salts, was not confirmed. The experiments were not carried far beyond the time after which oxygen begins to be evolved, through the reaction $H_2S_2O_8 + H_2O_2 = 2H_2SO_4 + O_2$, but it was shown that the velocity of this reaction increases considerably with decreasing concentration of acid. Friend's results (T., 1906 **89**, 1092), which showed that the reaction is unimolecular, can be explained on the assumption that Caro's acid is first formed from persulphuric acid, and then reacts with hydrogen peroxide. Persulphuric acid probably does not itself react with hydrogen peroxide. E. H. R.

Determination of the Rate of Solution of Atmospheric Nitrogen and Oxygen by Water. III. W. E. Adeney and H. G. Becker (*Sci. Proc. Roy. Dublin Soc.*, 1920, **16** [N.S.] 143—152).—A continuation of experiments previously reported (see A., 1919, ii, 104, 510). The rate of solution of air in quiescent water under laboratory conditions was determined. The results show that the process of solution under these conditions consists in solution at the surface with slow mixing in the body of the liquid. The results are represented by a formula, $dw/dt = a - bw$ where w = total quantity of gas in solution at any moment, t = time and a and b are constants depending on the size of the apparatus. The water was contained in vertical tubes exposed to air. The rate of solution depends on the humidity of the air, being greater with dry than with moist air. J. R. P.

Very High Pressures and the Synthesis of Ammonia Georges Claude (*Bull. Soc. chim.*, 1920, [iv], **27**, 705—724).—A lecture delivered before the French Chemical Society and the Society for the Encouragement of National Industry. W. G.

Fractionation of Nitric Acid. Julius Baumann (*Chem. Zeit.* 1920, **44**, 678).—Experiments on the fractionation of nitric acid were made, using a litre flask fitted with a dephlegmator 200 cm. long, inclined at 45°, with a jacket for heating it to any desired temperature. A mixture of 250 c.c. of water and 250 c.c. of

nitric acid (D 1·4; 69·8%, the constant boiling mixture) was distilled with the dephlegmator heated at 100°, and there were obtained 250 c.c. of distillate, containing only 0·02% HNO_3, and 250 c.c. of residual nitric acid, 69·5% in strength. Practically complete separation was therefore obtained. In another experiment, 500 c.c. of 91·5% HNO_3 were distilled with the dephlegmator heated at 86°, the boiling point of pure nitric acid. There were obtained in the distillation flask 140 c.c. of 70·1% HNO_3, and in the receiver 350 c.c. of 100·5% HNO_3. Thus a practically complete separation into pure nitric acid and the constant boiling mixture, b. p. 123°, was obtained. E. H. R.

Reduction of Nitrites and Nitrates. OSCAR BAUDISCH and PAUL MAYER (*Biochem. Zeitsch.*, 1920, **107**, 1—42).—Nitrites are reduced quantitatively by excess of ferrous hydroxide in neutral and alkaline solution. In boiling solutions made alkaline with carbonates, nitrous oxide and ammonia are chiefly formed. In boiling alkali hydroxide solution, the nitrite is quantitatively reduced to ammonia. Alkali nitrates are reduced quantitatively by ferrous hydroxide in neutral solution and in alkaline solution containing 28% of sodium hydroxide. Starting with neutrality, the amount of nitrate reduced diminishes until the alkali content is 6·5% of sodium hydroxide, when a minimum is reached; beyond that limit, the amount reduced increases with the increase of alkali until the maximum is reached at the concentration of 28% of sodium hydroxide. Up to a concentration of 6·5% of sodium hydroxide, oxygen is necessary for the reduction. With higher alkali concentrations, reduction also takes place in the absence of oxygen. At an alkali concentration of 6·5% of sodium hydroxide, the amount of nitrate reduced is proportional to the amount of nitrate present in solution, and is in a condition of adsorption by the ferrous hydroxide. The above observations are utilised for the estimation of nitrites and nitrates separately and when together. S. S. Z.

Equilibrium of the Four-component System: Na_2SO_4, $NaHCO_3$, $(NH_4)_2SO_4$, NH_4HCO_3 and H_2O. KYOSUKE NISHIZAWA (*J. Chem. Ind. Tokyo*, 1920, **23**, 25—43).—To study the best condition for the manufacture of ammonium sulphate by the ammonia-soda process from sodium sulphate, detailed studies were made of the equilibrium of a system consisting of these four components, first 2-component, then 3-component, and finally 4-component systems being determined. Ammonium hydrogen carbonate was prepared for each experiment. The concentration of the sodium sulphate and the ammonium sulphate was determined by the barium chloride and the Kjeldahl methods, respectively, and that of both bicarbonates by titration, using methyl-orange as indicator. The results are tabulated in sixteen tables and two curves. The results obtained from invariant systems are as follows:

Solid Phases.	Composition of the solution in gram-mol. 1000 gram-mol. H_2O.			
	Na_2SO_4.	$(NH_4)_2SO_4$.	NH_4HCO_3.	$NaHCO_3$
$Na_2SO_4,10H_2O$	16·61	—	—	—
$(NH_4)_2SO_4$	—	10·05	—	—
NH_4HCO_3	—	—	42·52	—
$NaHCO_3$	—	—	—	18·5
$Na_2SO_4,10H_2O$; $NaHCO_3$.	14·18	—	—	12·75
$Na_2SO_4,10H_2O$; $Na_2SO_4,(NH_4)_2SO_4,4H_2O$	31·54	45·14	—	—
$Na_2SO_4,(NH_4)_2SO_4,4H_2O$; $(NH_4)_2SO_4$	13·74	94·86	—	—
$(NH_4)_2SO_4$; NH_4HCO_3	—	96·40	14·91	—
$NaHCO_3$; NH_4HCO_3	—	—	38·92	12·79
$Na_2SO_4,10H_2O$; $NaHCO_3$; $Na_2SO_4,(NH_4)_2SO_4,4H_2O$	26·22	45·86	—	12·84
$NaHCO_3$; NH_4HCO_3 ; $Na_2SO_4,(NH_4)_2SO_4,4H_2O$	12·46	67·08	—	20·90
NH_4HCO_3 ; $(NH_4)_2SO_4$; $Na_2SO_4,(NH_4)_2SO_4,4H_2O$	6·79	97·99	—	14·96

CHEMICAL ABSTRACTS.

Cæsium Bromate. C. R. McCROSKY and HAROLD D. BUE[illegible] (*J. Amer. Chem. Soc.*, 1920, **42**, 1786—1789).—The preparatio[n] of cæsium bromate is probably best carried out in acid solutio[n]. Cæsium bromate is a definite crystalline salt without water [of] crystallisation. Occluded water causes decrepitation. Its mel[t]ing point (not yet determined) is above that of potassium broma[te]. After fusion, the salt soon decomposes, evolving a large amount [of] oxygen and leaving a bromide. The solubility of the salt is 4[illegible] grams in 100 grams of water at 30°. J. R. P

A New Rubidium (Cæsium)–Silver–Gold Compound a[nd] its Application to the Microchemical Detection of G[old,] Silver, Rubidium, and Cæsium. ERICH BAYER (*Mona[tsh.],* 1920, **41**, 223—241. Compare Emich, A., 1919, ii, 171[)]. Characteristic crystalline precipitates are formed when solut[ions] of rubidium or cæsium chloride are mixed with gold and si[lver] solutions; rubidium–silver–gold chloride forms blood-red pr[isms] and platelets, whilst the cæsium compound crystallises in op[aque] cubes and stars. The composition of the compounds corresp[onds] with the formulæ $Ag_xAu_{2-x/3}Cl_6,3RbCl$ and $Ag_xAu_{2-x/3}Cl_6,3$[illegible] (where $0 \leq x \leq 6$), in which gold and silver are mutually re[place]able components. For rubidium, silver, and gold, the atomic [pro]portions observed are in the ratio 3:0·81—1·04:1·5—1·4, [whilst] for the cæsium compound the corresponding ratio is 3: 1·18:1·82—1·64. The limiting compounds, Ag_2CsCl_3 and Au_2[illegible] do not appear to have been prepared, but Marsh and Rhyme[illegible] 1913, **103**, 782) have examined the analogous substances, A[illegible] and Ag_2RbI_3.

The crystals are adapted to the microchemical identificat[ion of] gold, silver, rubidium, and cæsium, the smallest qua[ntities] recognisable in this manner being 0·1, 0·01, 0·1, an[d illegible] microgram respectively. H.

A New Rubidium (Cæsium)-Silver-Gold Compound and its Application to the Microchemical Detection of Gold, Silver, Rubidium and Cæsium. FRIEDRICH EMICH (*Monatsh.*, 1920, **41**, 243—252. Compare Bayer, preceding abstract; Emich, A., 1919, ii, 171).—A theoretical paper in which ideas are developed based on Bayer's observation that univalent silver and tervalent gold are mutually replaceable in the rubidium (cæsium)-silver-gold chlorides.

It is suggested that elements in general have a far greater power of mutual replaceability than has previously been assumed, and that this is frequently the cause of the great difficulty experienced in isolating absolutely pure substances. Elements in general may be classified as (1) isotopic elements, the separation of which is impossible by precipitation or crystallisation; (2) isomorphous elements, which can only be incompletely separated; and (3) readily separable elements. The *most general conception* of the union of two substances is obtained by regarding it as controlled by the two factors, affinity in the narrower sense, due to the attraction of the atoms or molecules caused by harmonic vibration, and cohesive forces in the sense of the entropy rule. Both influences are, in general, operative, but the first predominates in chemical compounds, the second in isomorphous and isotopic mixtures. Between the limiting cases, which are generally well defined, because the controlling factors are usually of a widely differing order of magnitude, there are a number of transition examples, such as the rubidium-gold-silver compounds. It should be noted that this hypothesis involves the consideration of the laws of constant and multiple proportions, like the gas laws, as only approximately accurate.

Bayer's compounds are discussed at length, and it is pointed out that the limiting compounds, $RbCl,2AgCl$ and $3RbCl,2AuCl_3$, are not known, and that the stability of the molecule is increased by the entrance of a third component, and that the heavier cæsium has a more marked effect than the lighter rubidium. Re-examination of the triple nitrites has proved that there is a greater tendency towards mutual replacement among the bivalent than among the univalent elements, but the phenomena are not so well defined as with Bayer's salts.

Contrary to the previous observation (Emich, *loc. cit.*), it is now found that the place of rubidium cannot be taken by potassium in the triple chloride, and the value of the method for the microchemical detection of cæsium and rubidium is thereby greatly enhanced. H. W.

Ammonium Silicate. IV. The Ageing and Transformation of Silicic Acid Gel and the Course of the Solution of Silicic Acid in Ammonia. ROBERT SCHWARZ and OTTO LIEDE (*Ber.*, 1920, **53**, [*B*], 1509—1518. Compare this vol., ii, 175; A., 1917, ii, 31; 1919, ii, 283).—The authors have examined the behaviour of silica gel when slowly dried at the ordinary temperature and are led to the conclusion that the age-

ng process consists in the condensation of $(SiO_2)_x$ to $(SiO_2)_{2x}$, and hat this occurs without any change in the appearance of the gel; 'urther changes in the system SiO_2–H_2O then occur, leading to he formation of $(SiO_2)_{3x}$, which is indicated by the incipient 'ormation of cloudy particles in the colourless, transparent mass. ?recisely similar phenomena are observed when the gel is lehydrated by being heated, but, for some unexplained reasons, a nuch greater loss of water appears to be necessary in this case before the end-point is reached.

The solubility of silicic acid in ammonia has been examined in modified manner, since it has been found that the older measurenents, in which glass vessels were used, are very greatly influenced y the alkali from the glass. The hydrated silica and ammonia re mixed in the quartz vessel which serves for the measurement f the electrical conductivity. After definite intervals, portions f the solution are filtered through paper, which retains suspended ilica, and the filtrates are passed through an ultra-filter to retain olloidal particles. The silica retained by the paper and that in he final filtrate are estimated. It is found that equilibrium is ttained after about seventy-two hours at 18°, and that the soluion contains 64% of the silica in true solution, 8% in colloidal olution, and 28% undissolved. The conductivity and solubility urves show that the amount of dissolved silica increases during he whole course of the experiment, whilst the colloidal silica radually diminishes in quantity. The former therefore grows at he expense of the latter, and it appears justifiable to conclude hat the formation of the colloidal solutiou is the primary process hich is followed by the production of the molecular solution.

H. W.

Solubility of Calcium Carbonate. YUKICHI OSAKA (*J. Tokyo 'hem. Soc.*, 1920, **41**, 453—468).—On the assumption that only a nall part of the carbon dioxide dissolved in water is combined with ne water, and that consequently carbonic acid is a much stronger cid than acetic acid, the author has recalculated the solubility roduct of calcium carbonate from the data of McCoy and Smith n the solubility of calcium carbonate under different carbon ioxide pressures, using $K=3\cdot50\times10^{-7}$, $K_2=4\cdot91\times10^{-11}$, and has btained the value $7\cdot24\times10^{-9}$. The number of gram-molecules f calcium carbonate dissolved by 1 litre of water (C) under any nown carbon dioxide pressure (P) is given by the formula

$$C=[Ca^{\cdot\cdot}]+(1-y)/2y[HCO_3'].$$

here $Ca^{\cdot\cdot}=(5\cdot24\times10^{-17}+2\cdot49\times10^{-12}P^{\frac{1}{3}}+2\cdot97\times10^{-8}P^{\frac{2}{3}})/$ $2\cdot91\times10^{-6}P)$ and $HCO_3'=(2\cdot61\times10^{-6}P)/(7\cdot24\times10^{-9}+1\cdot72\times$ $0^{-4}P^{\frac{1}{2}})$, and y=the degree of dissociation of calcium acetate aving the same concentration of acetate ion as the bicarbonate n.

CHEMICAL ABSTRACTS.

Monoclinic Double Selenates of the Copper Group. . E. H. TUTTON (*Proc. Roy. Soc.*, 1920, [*A*], **98**, 67—95).—The

four double selenates of the series $R_2M(SeO_4)_2,6H_2O$, in which M is copper and R is potassium, rubidium, cæsium, or ammonium, have been examined crystallographically. They form a group in the extensive series of isomorphous monoclinic double sulphates and selenates which have been examined by the author, and the four salts exhibit the same relationships one to another as in similar groups of potassium, rubidium, cæsium, and ammonium salts. As was found in the case of the double sulphates, so in the double selenates, the constants, both physical and morphological, of the salts of the copper group differ considerably in their absolute values from those of the magnesium, zinc, iron, nickel, and cobalt groups (A., 1919, ii, 346).

The salts all crystallise in the holohedral-prismatic class of the monoclinic system. Potassium copper selenate, $K_2Cu(SeO_4)_2,6H_2O$, $a:b:c=0{\cdot}7508:1:0{\cdot}5143$, $\beta=103°25'$, D_4^{20} 2·539. Rubidium copper selenate, $Rb_2Cu(SeO_4)_2,6H_2O$, $a:b:c=0{\cdot}7495:1:0{\cdot}5066$, $\beta=104°44'$, D_4^{20} 2·839. Cæsium copper selenate,

$$Cs_2Cu(SeO_4)_2,6H_2O,$$

$a:b:c=0{\cdot}7398:1:0{\cdot}4981$, $\beta=105°42'$, D_4^{20} 3·073. Ammonium copper selenate, $(NH_4)_2Cu(SeO_4)_2,6H_2O$, $a:b:c=0{\cdot}7476:1:0{\cdot}5150$, $\beta=105°30'$, D_4^{20} 2·223.

The optical constants of the crystals were determined, and for each salt the axial ratios of the optical indicatrix and the molecular refraction and dispersion were calculated. E. H. R.

Comparative Study of the Decomposition of a Dissociable Mercurous Chloride obtained from Mercuric Chloride and of the Ordinary Form. GAMBIER (*Ann. malad. vénér.*, **15**, 28—31; from *Chem. Zentr.*, 1920, iii, 331).—Duret's observations (A., 1919, ii, 232) are confirmed, and, by variation of the precipitating and reducing agent, it has been found possible to secure a more voluminous and still more readily dissociable preparation which is quite free from mercuric chloride. The separation of free mercury has been estimated colorimetrically. The preparation gives 2·0 times at 15°, 2·4 times at 30°, 2·66 times at 60°, and 1·5 times at 100° as much mercury as does ordinary calomel, and the equilibrium between eliminated mercury and the unchanged molecule is very rapidly attained. H. W.

Inflammation of a Mixture of Aluminium and Sodium Peroxide by means of Water. OTTO OHMANN (*Ber.*, 1920, **53**, [*B*], 1427—1429).—An intimate mixture of finely divided aluminium (1 gram) and sodium peroxide (4·3 grams) is readily inflamed with slight explosion by the addition of a few drops of water. The experiment is best adapted to lecture purposes by sprinkling a small quantity of the powder on the surface of water, when it forms a thin skin without becoming inflamed; subsequent addition of more powder is then accompanied by inflammation. The suitability of the specimen of sodium peroxide should be ascertained, as its quality is liable to considerable variation.

H. W.

The Oxidising Properties of Sulphur Dioxide. I. Irc Chlorides. WILLIAM WARDLAW, and FRANCIS HERBERT CLE (T., 1920, **117**, 1093—1103).

The Oxidising Properties of Sulphur Dioxide. II. Irc Phosphates. WILLIAM WARDLAW, SIDNEY RAYMOND CARTER, a FRANCIS HERBERT CLEWS (T., 1920, **117**, 1241—1247).

Oxydase-like Action of Some Complex Salts of Metal YUJI SHIBATA and KEITA SHIBATA (*J. Tokyo Chem. Soc.*, 1920, **4** 35—53. Compare Colin and Liévin, A., 1919, i, 430).—Using 0·001*M*-alcoholic solution of myricetin to indicate the oxydase-li action, the authors have examined about fifty complex salts cobalt, nickel, copper, zinc, cadmium, chromium, and iron, and fi that the most reactive salts are those containing strong acid radicl or metals which give unstable complex ions in aqueous solutio for example, 1:6-dichlorotetramminecobalt chloride (in 0·001 solution) produces a bright red or purple coloration instantl pentamminecupric sulphate less markedly, dichloroethylenediamir chromium chloride very feebly, and potassium ferro- or fer cyanide not at all.

The four factors which operate against the oxydase-like acti are (1) hydrogen ions, (2) inactive complex salts, (3) hydroxylamir mercuric chloride, and a few other substances, (4) heating 80—90°. Valency plays no part, the reaction depending wholly the instability of the salts in water.

The application of these active complex salts to lacquers haste drying to a marked degree. CHEMICAL ABSTRACTS.

Salts of Stannic and Plumbic Acids. HANS ZOCH (*Zeitsch. anorg. Chem.*, 1920, **112**, 1—66).—A study of stannat and plumbates was undertaken with the object of elucidating t so-called semi-colloidal state, with a critical discussion of which t paper opens. The methods for preparing and analysing alk stannates are described. Sodium stannate crystallises from sodiu hydroxide solutions at ordinary temperatures as the trihydra $Na_2Sn(OH)_6$; it is practically insoluble in 7·0*N*-sodium hydroxic When precipitated by sodium hydroxide at 0° or by alcohol at or ordinary temperatures, it forms the tetrahydrate,

$$Na_2Sn(OH)_6,H_2O.$$

The solubilities of the two hydrates were determined between – and 50°; that of the trihydrate, the less soluble salt, which may regarded as an "anhydride," diminishes with increasing tempe ture, whilst that of the tetrahydrate increases. The transition poi was difficult to determine by the dilatometric method, but fr the solubility curves appears to be close to –5°. The trihydr forms a eutectic with water at –11°, the tetrahydrate at –7° addition, a third hydrate, approximating to $Na_2Sn(OH)_6,18H_2$ was discovered, which has a transition point to the "anhydride" 1°. The hydrolysis of sodium stannate in aqueous solutions

studied by means of potential measurements. In normal solutions the hydrolysis is about 2·7%, and appears to be complete at a dilution of $1/3000N$. In normal solutions of the stannate the extent of hydrolysis gradually increases with time. This phenomenon is discussed in connexion with similar observations in the case of other colloidal solutions and of solutions of tin tetrachloride. There is no evidence of adsorption of alkali by sodium stannate under any conditions.

Lithium stannate forms an "anhydride," $Li_2Sn(OH)_6$, isomorphous with the sodium salt, and also a dihydrate of this salt, $Li_2Sn(OH)_6,2H_2O$ The solubilities of both salts were determined between 28° and 80°. The two curves are approximately parallel, the solubilities increasing with the temperature; the transition point could not be fouud, but is probably below 100°. Potassium stannate forms an "anhydride," $K_2Sn(OH)_6$, and also a mono- and di-hydrate of this salt. The solubilities are greater than those of the sodium and lithium salts.

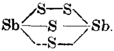
In the course of a long discussion on the chemistry of stannic oxide from the colloidal point of view, the following points are elucidated. The low crystallisation velocity of the oxide, resulting from its slight solubility, facilitates its assumption of the colloidal state. The "ageing" of the colloid is accelerated or retarded by various influences, particularly by accompanying salts in solution. Coagulation, that is, the coalescence of the bounding surfaces of the colloidal particles in solution, is retarded by the electrostatic charge on the particles.

The work was also extended to the plumbates. Sodium plumbate was prepared by dissolving freshly precipitated lead peroxide, in small quantities at a time, in boiling concentrated ($8—10N$) sodium hydroxide solution. The salt is very sparingly soluble in this solution, and separates in crystals which appear to be isomorphous with sodium stannate. Although the analyses of the crystals always showed excess of Na_2O, their composition is taken to be $Na_2Pb(OH)_6$. Lithium plumbate was also prepared, and appeared, from its crystalline form, to be isomorphous with the sodium salt. The properties of plumbic acid are discussed from the colloidal point of view. E. H. R.

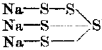
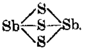
Antimony Pentasulphide (Sulphur auratum). F. KIRCHHOFF (*Zeitsch. anorg. Chem.*, 1920, **112**, 67—80).—The ordinary golden antimony sulphide is described in the literature as consisting of a mixture of pentasulphide and trisulphide, with more or less free sulphur. The purest form of the substance contains about 8% of sulphur, which can be extracted with carbon disulphide or acetone, the residue having a composition corresponding with the formula Sb_2S_4. This form is obtained by the action of dilute acids on Schlippe's salt, according to the equation $2Na_3SbS_4 + 6HCl \longrightarrow Sb_2S_4 + S + 6NaCl + 3H_2S$. It is shown in the present paper that antimony pentasulphide has no existence, but that golden antimony sulphide is a mixture of Sb_2S_4 with from 0 to 50% Sb_2S_3 and a vary-

ing amount of free sulphur, according to the method of prepara tion. The compound Sb_2S_4 has been prepared in a pure state fron zinc thioantimonate. The latter salt, $Zn_3Sb_2S_8$, was prepared b the interaction of Schlippe's salt and zinc chloride. It formed chrome-yellow precipitate, which when dried and ground had bright orange-red colour. The crude substance contained abou 6·7% of extractable sulphur, and after removal of this, its com position corresponded exactly with the above formula. The zin thioantimonate is decomposed by dilute acids according to th equation $Zn_3Sb_2S_8 + 6HCl \longrightarrow Sb_2S_4 + 3ZnCl_2 + H_2S_2 + 2H_2S$. Ana lysis of the orange-red residue from this reaction showed it to hav the composition Sb_2S_4, the same as that of the pure extracte orange form of golden antimony sulphide.

The sulphide Sb_2S_4 is to be regarded as a special case of com pounds of the type $M_x(SbS_4)_y$, in which M becomes Sb and $x=$ The structural formula suggested for the compound i



For the corresponding sodium salt (Schlippe's salt

the structure becomes  and a corresponding formul is suggested for the zinc salt. The colour of the compound Sb_2S and of the thioantimonates of the heavy metals is attributed to th presence of closed ring systems in the structure of these compound The sodium salt, in which there is no closed ring, is colourless. Th red antimony trisulphide probably has the structure 

E. H. R.

Revision of the Atomic Weight of Bismuth. Analys of Bismuth Chloride. O. Hönigschmid and L. Birckenba (*Zeitsch. Elektrochem.*, 1920, **26**, 403—408).—See this vol., ii, 54

The Binary System Lead–Bismuth. W. Herold (*Zeits anorg. Chem.*, 1920, **112**, 131—154).—The limits of the eutec range in the lead–bismuth alloys have been determined by differe observers, generally by thermal methods, with divergent resul These limits have now been investigated by studying the electri conductivity and hardness of the alloys and their microscopic str ture. Special precautions were taken to obtain uniform specim by careful annealing. The conductivity experiments, which w made at 123° and 0°, indicated for the limit of solubility bismuth in lead, 17·5 to 18·5% Bi, and for the solubility of lead bismuth, 1·6% Pb. The interpretation of the results of the hardn experiments was uncertain owing to the influence of the treatm which any particular sample had undergone on its hardness. T hardness–composition curve had a wave-form with an inflex corresponding approximately with the eutectic point. The ha

ness of the eutectic does not appear to derive additively from that of the two series of mixed crystals. The curve indicates the mixed crystal limit on the lead side at about 17—18% Bi. The microscopic experiments showed that a sample containing 40% Bi contained no trace of eutectic after annealing eight hours at 124°. Alloys with more than 40% Bi showed eutectic after thirty hours at 40°. It is concluded that the two limits for the eutectic are 40% Bi and 0·2—0·5% Pb. E. H. R.

Normal Bismuth Tungstate and Molybdate: their Relations to the Corresponding Lead Compounds. F. ZAMBONINI (*Gazzetta*, 1920, **50**, ii, 128—146).—The author has prepared and examined, especially crystallographically, normal bismuth tungstate and molybdate, and has subjected the two systems, $PbWO_4-Bi_2(WO_4)_3$ and $PbMoO_4-Bi_2(MoO_4)_3$, to thermal analysis.

Normal bismuth tungstate, $Bi_2(WO_4)_3$, is dimorphous, and crystallises in (1) the monoclinic system, $a:b:c=1·006:1:1·520$, $\beta=90°34'$, $D^{7·5}$ 8·24, and (2) the tetragonal system, $a:c=1:1·566$. The latter phase corresponds perfectly with the tetragonal phase both of the normal molybdates and tungstates of the elements of the yttrium and cerium group, as well as of those of the *isomorphogenic* elements of the calcium–strontium–barium–lead group, the value of $a:c$ in these compounds varying from 1:1·542 to 1:1·623. The monoclinic form is distinctly pseudo-tetragonal, the axial ratios differing but little from 1:1:1·566 and the value of β but little from 90°. This monoclinic form exhibits undeniable crystallographic resemblances to raspite, the monoclinic form of lead tungstate, but the tetragonal bismuth tungstate shows far closer resemblances to stolzite, the tetragonal form of lead tungstate.

Normal bismuth molybdate, $Bi_2(MoO_4)_3$, was obtained only in the tetragonal form, $a:c=1:1·5636$, D^{15}_{15} 6·07, the crystallographic constants and the molecular volume differing little from those of the molybdates of the cerium metals and of lead.

Monoclinic bismuth tungstate has m. p. 832°, tetragonal bismuth molybdate, m. p. 643°, and lead tungstate and molybdate, m. p. 1130° and 1065° respectively. For the system $Bi_2(WO_4)_3-PbWO_4$ the melting-point diagram has the form characteristic for binary mixtures, either forming no solid solutions or exhibiting extremely limited mutual solubility in the solid state. The crystallisation curve first falls rapidly from 1130° to a eutectic point at about 813° corresponding with about 73 mol. % of $Bi_2(WO_4)_3$, and then rises directly to 832°. The system $PbMoO_4-Bi_2(MoO_4)_3$ shows quite similar behaviour, the crystallisation curve descending rapidly from 1065° to a eutectic at about 615°, corresponding with about 71·5 mol. % of $Bi_2(MoO_4)_3$, and then rises directly to 643°. With both systems the form of the curve of eutectic arrests indicates that the eutectic disappears completely only in the pure components.

T. H. P.

Mineralogical Chemistry.

Zinc-blende in the Basalt of Bühl, near Cassel. W. EITEL (*Centr. Min.*, 1920, 273—285).—Black zinc-blende intimately associated with quartz, and sometimes pyrrhotite or pyrites, occurs as enclosures in the basalt. Analyses show it to be of the marmatite variety with FeS : ZnS = 1 : 4 and 1 : 3 in the two analyses respectively:

	Fe.	Mn.	Zn.	Cd.	S.	Gangue.	Total.	Sp. gr.
I.	12·28	trace	52·02	—	32·08	3·52	99·90	—
II.	19·50	trace	48·08	trace	31·79	0·98	100·35	4·033

The presence of the mineral is attributed to the basalt breaking through a mineral-vein and enveloping fragments of the same. It is supposed that the original pyrites was largely dissociated to ferrous sulphide, which was partly absorbed by the zinc sulphide the remainder being represented by the pyrrhotite. L. J. S.

Ultrabasite, a New Mineral from Freiberg, Saxony V. ROSICKÝ and J. ŠTĚRBA-BÖHM (*Zeitsch. Kryst. Min.*, 1920, 55 430—439; *Rozpr. České Akad.*, 1916, **25**, *No.* 45).—The black crystals with metallic lustre and black streak are orthorhombic ($a : b : c = 0·988 : 1 : 1·462$) with a tetragonal habit. H 5, D 6·026 They are associated with quartz, rhodochrosite, galena, and proustite on gneiss. Analysis gave:

Sb.	Ag.	Pb.	Cu.	Fe.	Ge.	S.	Total.
4·60	22·35	54·16	0·47	0·25	2·20	16·15	100·18

agreeing with the ultrabasic formula $Sb_4Ag_{22}Pb_{28}Ge_3S_{53}$. The finely powdered mineral is slowly decomposed by digestion with hydrochloric or nitric acid, with separation of some sulphur. It is readily decomposed by fusion with alkali carbonates and nitrate and the solution gives with the Marsh test a characteristic germanium mirror. Germanium was also detected in cylindrite from Bolivia by this method. A rough separation of germanium and antimony was effected by carefully acidifying with dilute sulphuric acid the solution of the sulphides in sodium sulphide, the bulk of the germanium remaining in solution whilst antimony was precipitated. L. J. S.

Minerals from Tsumeb, S.W. Africa. O. PUFAHL (*Centr. Min.*, 1920, 289—296).—*Zinciferous tennantite*, occurring either alone (anal. I, D 4·61) or intimately associated with galena (II), massive, with black colour and greenish lustre and a dark cherry-red streak.

	S.	As.	Sb.	Cu.	Zn.	Pb.
I.	23·35	17·94	4·66	43·60	9·24	0·22
II.	22·05	19·65	4·03	43·19	9·27	0·08

	Fe.	Ag.	Au.	SiO_2.	Total.
I.	0·03	0·11	0·01	0·97	100·13
II.	0·17	n.d.	n.d.	0·81	99·85

Mimetite occurs in the secondary zone as compact masses and as almost colourless, prismatic crystals (anal. III); it is frequently altered to bayldonite. Mottramite is abundant as compact or cellular masses with sometimes a reniform (IV) or botryoidal (V) surface. It is dark olive-green, with a pale yellow streak, and is readily soluble in hot dilute hydrochloric acid with evolution of chlorine. Full details of the method of analysis are given; the results agree with $4(Cu,Pb)O,V_2O_5,2H_2O$, in which Cu : Pb = 1 : 1. Cuprodescloizite as crusts of small, dark olive-green crystals showing pyramidal points gave VI, corresponding with $4(Cu,Pb)O,V_2O_5,H_2O$, in which PbO : (CuO + ZnO) = 1 : 1. A new lead copper arsenate, named *duftite*, forms pale olive-green crusts of small, indistinct crystals (resembling olivenite in form) on crystals of azurite. It is soluble in hot dilute hydrochloric acid. Anal. VII corresponds with $2Pb_3(AsO_4)_2,Cu_3(AsO_4)_2,4Cu(OH)_2$. The mineral contains no trace of chlorine or phosphoric acid, and consequently it has probably not been derived from mimetite, although it is sometimes associated with remains of this.

	PbO.	CuO.	ZnO.	MnO.	V_2O_5.	As_2O_5.	SiO_2.	H_2O.	Total.	Sp. gr.
III.	67·31	trace	—	—	—	23·12	—	—	99·76*	6·98
IV.	54·70	18·75	0·19	trace	21·05	1·25	0·28	3·93	100·15	5·93
V.	53·33	19·50	0·16	trace	19·20	3·04	0·70	3·92	99·85	5·90
VI.	54·90	16·27	3·51	trace	21·69	1·36	0·07	2·33	100·13†	6·19
VII.	50·10	19·32	0·46	—	—	26·01	0·44	2·73	99·81‡	6·19

* Incl. $PbCl_2$ 9·33 (Cl 1·38). † Also Fe_2O_3 trace. ‡ Incl. CaO 0·75

L. J. S.

Phosphate-bearing Pegmatites from Bavaria. H. LAUBMANN and H. STEINMETZ (*Zeitsch. Kryst. Min.*, 1920, **55**, 523—586).—Phosphate-bearing pegmatites, similar to those near Limoges in France and Branchville in Connecticut, are described from five localities in Bavaria. The anhydrous phosphate minerals, fluormanganapatite, triplite, triphylite, and triploidite, are present as original constituents of the pegmatite, and by their alteration by thermal waters they have given rise to a great variety of well-crystallised hydrated phosphate minerals. The latter include the iron (ferrous and ferric) phosphates, dufrenite, beraunite, strengite, phosphosiderite, cacoxenite, and vivianite; manganiferous phosphates containing also iron and alkaline earths, such as fairfieldite, phosphophyllite, phosphoferrite, xanthoxenite, and kreuzbergite; rarely manganese ferrous phosphates of the heterosite-purpurite series; simple manganese phosphates are here, however, absent. Analyses are given of the following: I, altered triplite from Plössberg; the fresh material contains P_2O_5, 34·13%. II, triplite from Pleystein. III, triplite from Hagendorf. IV, triphylite from Hagendorf. V, strengite as good violet-blue crystals ($a:b:c$ = 0·8663 : 1 : 0·9776) from Pleystein; formula $Fe_2O_3,P_2O_5,8H_2O$. VI, phosphosiderite as almond-blossom-red crystals ($a:b:c$ = 0·5456 : 1 : 0·8905) from Pleystein; formula $Fe_2O_3,P_2O_5,7H_2O$.

VII, *phosphophyllite*, a new species, forming colourless or pale blue, monoclinic crystals ($a : b : c = 1\cdot0381 : 1 : 1\cdot7437$, $\beta = 89°32'$) with

	P_2O_5.	Fe_2O_3.	FeO.	MnO.	Li_2O.	F.	Insol.	H_2O.	Total.
I.	19·73	—	41·60	31·03	—	6·28	1·03	—	—
II.	33·14	—	33·51	25·42	—	6·77	0·46	—	—
III.	31·89	—	35·50	28·66	—	7·29	0·83	—	—
IV.	44·43	—	35·06	11·40	8·59	—	0·60	—	—
V.	38·24	43·40	—	—	—	—	—	18·89	100·53
VI.	37·71	44·38	—	—	—	—	—	17·31	99·40

perfect micaceous cleavage, D 3·081, from Hagendorf; formula $P_2O_5,2\frac{1}{2}R''O,\frac{1}{2}K_2O + \frac{2}{3}SO_4Al-OH + 3H_2O$ or

$$3R_3P_2O_8 + 2AlOH\cdot SO_4 + 9H_2O.$$

VIII, *phosphoferrite*, a new species, from Hagendorf, occurring as cloudy-white or greenish, crystalline masses with greasy lustre.

	P_2O_5.	SO_3.	Al_2O_3.	FeO.	CaO.	MgO.	K_2O.	Ign.	Insol.	Total.
VII.	25·85	9·17	6·12	13·55	5·12	12·04	8·50	13·17	3·66	98·09*
VIII.	35·10	0·75	0·61	40·35	5·30	6·20	0·55	4·67	1·94	— †

* Including BaO 0·91. † Also MnO 2·46, Na_2O 0·25, SiO_2 1·03.

D 3·156. Formula $H_3PO_4,3PO_4,4\frac{1}{2}R''$ or $H_6R_9''(PO_4)_8$. The primary apatite contains P_2O_5 42·61, MnO 4·93, and no chlorine, and is therefore described as *fluormanganapatite*. *Kreuzbergite*, a new species from the Kreuzberg at Pleystein, forms small, colourless to pale yellow, orthorhombic crystals ($a : b : c = 0\cdot3938 : 1 : 0\cdot5261$), D 2·139, and consists essentially of hydrated aluminium phosphate with some iron, calcium, and manganese. *Xanthoxenite*, a new species from Rabenstein, occurring as small, wax-yellow, monoclinic crystals, D 2·844, intimately associated with dufrenite and cacoxenite; it is a basic ferric phosphate (P_2O_5, 32·61; loss on ignition, 16·10%) with some manganese and calcium. L. J. S.

Pickeringite from Opálbánya, Hungary. VIKTOR ZSIVNY (*Zeitsch. Kryst. Min.*, 1920, **55**, 629—631).—Yellowish-white, fibrous material with silky lustre gave (also traces of MnO, Na_2O, NH_3, P_2O_5):

SO_3.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	FeO.	H_2O.	Total.
36·62	9·52	4·04	4·06	0·70	0·23	45·42	100·59

agreeing with the usual formula, $(Al,Fe)_2(Mg,Ca,Fe)(SO_4)_4,22H_2O$. Together with other sulphates, the mineral is of recent formation in the levels of the opal mines, having been formed by the decomposition of the small crystals of iron-pyrites present in the hypersthene-andesite matrix of the opal. L. J. S.

Minerals from Madagascar and the Urals. RENÉ CHARLES SABOT (*Thèse, Univ. Genève*, 1914, 1—138; from *Jahrb. Min.*, 1920, i, Ref. 138—142).—Crystallographic and optical determinations, usually with analyses, are given for a number of minerals. Most of the data have been previously published (Duparc, A., 1910, ii, 221; 1913, ii, 782; 1914, ii, 664, etc.), but the following

analyses appear to be new. I, Muscovite, plumose mica, from Ampatsakana, Madagascar. II, Spessartite crystals from Takovaya, Urals. Blue apatite, occurring with rubellite and felspar at Antsongombato, Madagascar, gave: P_2O_5, 40·09; CaO, 54·45; MnO, 1·80; Cl, 0·20; F [3·46]; D 3·2013.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.
I.	44·35	37·40	—	5·30	0·30	0·19
II.	35·12	20·40	2·06	6·78	33·16	2·10

	MgO.	K_2O.	H_2O.	Total.	Sp. gr.
I.	1·67	5·94	5·29	100·44*	2·8908
II.	0·15	—	—	99·77	4·1577

* Also TiO_2, Na_2O traces.

L. J. S.

Optical Characters of Epidote. M. GOLDSCHLAG (*Tsch. Min. Mitt.*, 1917, **34**, 23—60; from *Jahrb. Min.*, 1920, i, Ref. 135—137).—Optical determinations were made on clinozoisite and epidote from various localities, and the results correlated with the chemical composition (percentage of ferric iron reckoned as an iron-epidote molecule). The following new analysis, by KAROLINE LUDWIG, is given of epidote from Pfarrerb, Zöptau, Moravia:

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total.
38·34	26·11	9·67	1·07	23·93	0·34	n.d.	99·46

L. J. S.

Andesine from Hohenstein, Kremsthal, Lower Austria. O. GROSSPIETSCH (*Sitzungsber. Akad. Wiss. Wien*, 1918, **127**, 439—447; from *Jahrb. Min.*, 1920, i, Ref. 132).—Analysis of crystals gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Na_2O.	Ign.	Total.	Sp. gr.
59·98	24·67	0·54	7·26	trace	7·36	0·09	99·90	2·67

corresponding with $Ab_{65}An_{35}$. The optical constants are given.

L. J. S.

Analytical Chemistry.

Qualitative Chemical Analysis. V. MACRI (*Boll. Chim. Farm.*, 1920, **59**, 385—389).—The author gives a scheme according to which the metals are detected approximately in the opposite order to that of the method commonly employed, one advantage of this procedure being that it allows of the use of fixed alkalis or their salts. [See *J. Soc. Chem. Ind.*, 1920, November.]

T. H. P.

The Analysis of Aqueous Solutions with the Aid of th Refractometer. MAX DE CRINIS (*Zeitsch. physiol. Chem.*, 192 **110**, 254—265).—The refractive index of salt solutions which not manifest the phenomenon of molecular attraction is in dire linear proportion to the percentage of the concentration of th salt in the solution. On establishing this relation between th refractive index and the concentration of a solution, it is possib to calculate the percentage of the concentration by means of th formula $y = (nDX\% - 1{\cdot}33320)/b$ ($nDX\%$ = refractive index of X solution, b = refractive index of 1% solution of the same sal 1·33320 = refractive index of distilled water). The refractive ind of a mixture of equal parts of various salt solutions is equal the sum of the refractive indices of the solutions which make up. If by mixing these salts some substance is precipitated, th refractive index of the precipitated salt can be obtained by su tracting the refractive index of the remaining solution from th sum of the refractive indices of the component solutions. Th ion content of the aqueous solution can therefore be calculated, follows: $P = (nDRX\% - nDOX\%)/K$. P = percentage; $nDRX\%$ refractive index of X%-solution obtained by calculation; $nDOX\%$ refractive index observed after precipitation; $K = nDR1\%$ $nDO1\%$ of a 1% solution. S. S. Z.

A Simple Method for Titrating Electrometrically to Desired End-point in Acid-alkaline Reactions. P. KLOPSTEG (*Science*, 1920, **52**, 18—19).—The hydrogen electro can be utilised to compare a known standard solution with o of unknown p_H value. From the curves of Sörensen (*Ergeb Physiol.*, 1912, **12**, 393) or the formulæ of Clark and Lubs (A 1916, ii, 44) is selected the solution with p_H value correspondi with the point to which it is desired to titrate. This solution placed in connexion (by means of a bridge of potassium chlori solution) with the unknown, each being provided with a hydrog electrode. The two electrodes are connected by a tapping k and high-resistance galvanometer. Titration to an end-point effected by merely adding solution until, on tapping the key, deflection is observed, showing equal hydrogen-ion concentrations the two solutions. The accuracy is limited by that of the p_H val of the standard solution. CHEMICAL ABSTRACTS.

The H-ion Concentration of some Standard Solutions Various Temperatures. L. E. WALBUM (*Biochem. Zeitsc* 1920, **107**, 219—228; *Compt. rend. Soc. Biol.*, 1920, 8 707—709).—The H-ion concentration of mixtures of glycine a sodium hydroxide, borate and hydrochloric acid, and borate a sodium hydroxide increases with increased temperature betwe 10° and 70°. The reverse is the case with a citrate and sodi hydroxide mixture. In the former three mixtures, the alteration more marked in the alkaline mixtures, but diminishes with t diminution of the alkalinity of the mixtures. S. S. Z.

Use of Ethyl Ether in Iodometric Estimations. L. GEBET (*Mitt. Lebensmittelunters. Hyg.*, **11**, 67—68; from *Chem. Zentr.*, 1920, iv, 354).—Commercial ethyl ether can liberate large quantities of iodine in consequence of the presence of peroxidised substances. Such ether should be dehydrated with calcium chloride and subjected to prolonged treatment with metallic sodium, or shaken with concentrated alkali thiosulphate, rapidly dried over calcium chloride, and distilled. H. W.

Extensive Employment of Arsenious Acid in Volumetric Analysis. R. NAMIAS (*Giorn. chim. ind. applicata*, 1920, **2**, 176).—A reply to de Bacho (this vol., ii, 188).

CHEMICAL ABSTRACTS.

Application of the Thermal Conductivity Method to the Analysis of Complex Mixtures of Gases. E. R. WEAVER and P. E. PALMER (*J. Ind. Eng. Chem.*, 1920, **12**, 894—899).—The thermal conductivity method can only be applied quantitatively when the probable identity and amounts of constituents likely to be present in a gaseous mixture are known. For estimation of a constituent by comparison with a standard gas, air is the most suitable standard for mixtures with low conductivity, and hydrogen for those with high conductivity. This is suitable for estimating hydrogen in air, the relative proportions of hydrogen and ammonia in gases for synthetic ammonia processes, and impurities in hydrogen. In other cases, such as the estimation of chlorine, hydrogen chloride, sulphur dioxide, acetylene, and water vapour in various gaseous mixtures, the results are calculated by comparing the conductivities before and after a chemical reaction. Thus, the total amount of atmospheric gases in a hydrogen-filled balloon may be estimated by applying the method before and after the reaction of the oxygen with the hydrogen. Similarly, methane in air may be estimated by the difference in the results obtained before and after passing the air over hot copper oxide. Another modification is to add a gas to a mixture prior to the reaction. For example, in estimating oxygen in flue gas, hydrogen is first added, and the oxygen removed by combustion. The difference in the conductivities of the residual excess of hydrogen and nitrogen in the mixture is too small to affect the accuracy of the results for oxygen. In like manner, successive combustions with oxygen and hydrogen may be used for certain mixtures, as, for example, in estimating carbon monoxide in the presence of large amounts of hydrogen. C. A. M.

Estimation of Chlorine in Blood. M. RODILLON (*Presse méd.*, **28**, 85—86; from *Chem. Zentr.*, 1920, iv, 315—316).—A solution of trichloroacetic acid (1 : 5; 15 c.c.) is added slowly and with stirring to an equal volume of the well-centrifuged serum, and the mixture is passed through a folded filter. 11·7 c.c. of the filtrate (a portion is reserved for the estimation of carbamide) are treated with $N/10$-silver solution (10 c.c.), distilled water

0—60 c.c.), and finally with ferric alum solution (10 c.c.); the ixture is thoroughly agitated and titrated with $N/10$-ammonium iocyanate solution until the red coloration persists. H. W.

A New Method for the Estimation of Bromine. . HARTWICH (*Biochem. Zeitsch.*, 1920, **107**, 202—206).—The ine is incinerated with sodium carbonate and acidified with lphuric acid. Chlorine water is added and the liberated bromine extracted with chloroform. The bromine is calculated from the iantity of chlorine used up. 347 Mg. of sodium bromide were timated by this method in 100 c.c. of bromine-free urine with ı error of about 3%. S. S. Z.

Use of Barcroft's Differential Apparatus. R. WERTHEIMER iochem. Zeitsch., 1920, **106**, 1—11).—Replacement of Barcroft's rmula (A., 1908, ii, 319, 529) by that of Münzer and Neumann ., 1917, i, 520) gives for the gas volume a value higher by about 5%, or, if the barometric pressure is corrected for the pressure the water vapour, lower by about 0·4%. Use of Barcroft's rmula and neglect of the water-vapour pressure correction is ence recommended. Determination of the constants of the paratus is described. T. H. P.

Investigations on Alveolar Gas Pressures by a New lethod. PIUS SUPERSAXO (*Biochem. Zeitsch.*, 1920, **106**, 56—82). -The author has tested a new method, devised by Asher, for vestigating alveolar air which permits of the estimation of both ie carbon dioxide and the oxygen. The analysis is carried out y means of the Bunte burette, and as it requires 100 c.c. of air, laldane and Priestley's method (A., 1905, ii, 400) is modified so s to yield increased quantities of the alveolar air. The method fully described. T. H. P.

Estimation of Neutral Sulphur in Urine. PAUL LIEBESNY *Biochem. Zeitsch.*, 1920, **105**, 43—48).—Estimation of the ulphur in sulphosalicylic acid solution by precipitation as enzidine sulphate was found to yield results 8—10% in excess of he true value, owing to the presence of sulphur compounds in he gas employed as source of heat during the operations. The uthor has therefore modified Raiziss and Dubin's method of stimating the total sulphur in urine (A., 1914, ii, 671), use being iade of an electric combustion furnace. The total sulphates in rine may be estimated by Rosenheim and Drummond's method A., 1914, ii, 485), the difference between total sulphur and total ulphates representing neutral sulphur. T. H. P.

Volumetric Method for the Estimation of Acids and lases which yield Insoluble Salts. HANS TH. BUCHERER *Zeitsch. anal. Chem.*, 1920, **59**, 297—302).—For the estimation f sulphuric acid, the hot solution containing the latter is titrated rith N-barium chloride until the precipitation of barium

sulphate appears to be complete. A small portion of the solution is then filtered, and the filtrate divided into two portions, which are tested with a drop of barium chloride solution and a drop of dilute sulphuric acid respectively. If a precipitate is obtained with barium chloride, the titration is continued, and the solution again tested after filtration. In this way, the amount of barium chloride necessary for the precipitation of the sulphuric acid is ascertained approximately. The titration is then repeated on a fresh portion of the original solution, the final titration being made with N/10-barium chloride solution. Similar methods of titration may be used for the estimation of calcium (as oxalate), magnesinm (as ammonium magnesium phosphate), etc.

W. P. S.

A Little-known Still-head for Kjeldahl Distillation. A. Prange (*Chem. Zeit.*, 1920, **44**, 681).—To guard against frothing over during distillation of ammonia when estimating nitrogen by the Kjeldahl process, the glass tube leading from the distillation flask to the receiver is inclined in an upward direction for some distance from the safety bulb. This gives additional security should the bulb become filled with froth. E. H. R.

The Technique for the Estimation of the Residual Nitrogen in Blood. Joh. Feigl (*Biochem. Zeitsch.*, 1919, **101**, 62—73).—A theoretical paper. Folin and Wu's method (A., 1919, ii, 308) is considered an improvement on other methods.

S. S. Z.

Colorimetric Estimation of Ammonia, Nitrites, and Nitrates. I. M. Kolthoff (*Pharm. Weekblad*, 1920, **57**, 1253—1264).—In addition to the difficulty that colorimetric determinations are not accurate to within 5 to 10%, irregularities occur in practice from the influence of such factors as the quantity of reagent, the temperature, the time, the presence of retarding substances, etc. In the quantitative estimation of traces of ammonia by means of Winkler's reagent, which will detect 0·1 mg. NH_4 per litre, time was not found of great importance, the colour being at its maximum for different concentrations of the reagents after fifteen minutes in all cases. The quantity of reagent used has a marked effect, 0·3 c.c. of Winkler's reagent producing the same colour with 50 c.c. of a solution containing 0·6 mg. NH_4 per litre as 0·5 c.c. produced with the same volume of a solution containing 0·4 mg. NH_4 per litre. The strongest colour was obtained by adding 0·5 c.c. of the reagent to 50 c.c. of the ammoniacal solntion. The presence of excess of potassium iodide depresses the sensitiveness enormously; the presence of 0·3 c.c. N-KI with 1 c.c. of the reagent and 50 c.c. of a solution containing 10 mg. NH_4 per litre reduced the colour to equality with that given by 50 c.c. of a solution containing 0·35 mg. NH_4 with 1 c.c of the reagent, whilst 0·6 c.c. N-KI prevented the formation of the colour completely. The influence of a small excess of potassium

iodide varies with the concentration of the reagents. Bromides and thiocyanates have a preventive effect, although not so great as iodides. Chlorides have very little effect unless in large quantity. Sulphates have little effect on the colour, but hasten the separation of the orange precipitate. Secondary phosphates weaken the colour, whilst addition of excess of alkali hydroxide inhibits it entirely, as also does cyanide. A very satisfactory reagent, capable of detecting 0·1 mg. NH_4 per litre, is mercury sodium chloride in weak alkaline solution, which gives a white opalescence permitting of nephelometric estimation.

The recent work of Frederick (A., 1919, ii, 371) and Massink (*Water*, **3**, 89) on the phenol–sulphuric acid method of estimating nitrates is examined, and the influence of traces of chlorides shown by Massink to be necessary is confirmed, although the quantitative effect is greater than Massink stated. The test is best carried out by adding to the working solution 0·5 c.c. *N*-NaCl, evaporating to dryness, adding to the residue 2 c.c. of phenolsulphuric acid, and warming for twenty minutes on the water-bath. The liquid is then diluted and rendered ammoniacal according to the procedure of Frederick. In the new form, the reaction is quantitative, the colour being proportional to the amount of nitrate present. Nitrites have very little effect on the reaction in this form. The brucine–sulphuric acid method was also examined, but no quantitative results could be obtained.

The Griess-Romijn method for the colorimetric determination of nitrite is also examined, and modifications are recommended. If 100 c.c. of the reagent be added to 50 c.c. of the solution under test, and the mixture warmed to 55—60° for five minutes, the maximum colour is reached at once on cooling. Since alkalis inhibit strongly, a hard water should first be made acid with acetic acid. S. I. L.

Estimation of Ammonia in Urine, in Serous Liquids, and in the Oxidised Liquid of the Kjeldahl Method. ARNOLD HAHN and ELISABETH KOOTZ (*Biochem. Zeitsch.*, 1920, **105**, 220—228).—Using Hahn's modification of the Krüger, Reich, and Schittenhelm method, all the ammonia is expelled in five minutes from a solution containing 0·04 gram of ammonia as ammonium sulphate, 25 c.c. of water, 10 grams of sodium chloride, 1 gram of sodium carbonate, and 30 c.c. of 96% alcohol if the distillation flask is heated in a boiling-water bath and the distillation is carried out in the maximum vacuum given by a water pump. Under these conditions, carbamide (2 grams) yields no ammonia. Cooling of the receiver containing the standard acid for absorbing the ammonia is found to be unnecessary. Methods based on the above results are given for the estimation of ammonia in urine either free from, or containing, protein, in blood serum, and in the decolorised acid liquid of the Kjeldahl method. A special indicator containing sodium alizarinsulphonate and methylene-blue is used for titrating the alcoholic *N*/100-acid used in the case of blood serum. T. H. P.

The Conductometric Titration of Phosphoric Acid an its Salts. I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, **11** 165—171).—Phosphoric acid behaves as a strong acid, and cann be titrated conductometrically in concentrated solution (compa this vol., ii, 420). In dilute solution it can be titrated in exact the same way as a mono- or di-basic acid, the first equivale point being very sharp, the second less distinct. The conduct metric method of titration has the advantage over the indicat method that indicators give indistinct end-points in very dilu solutions of phosphoric acid. Secondary phosphates, for examp Na_2HPO_4, can be titrated with acids when the concentration less than 0·01 molar. When the concentration is greater, t break in the conductivity curve at the point corresponding wi primary phosphate is indistinct, owing to the dissociation of ph phoric acid. Secondary phosphates cannot be titrated with alka on account of the hydrolysis of the tertiary phosphates. Dilu solutions of pyrophosphates can be satisfactorily titrated with ac to the secondary salt. The break corresponding with the tertia salt is indistinct. E. H. R.

Estimation of Carbon Dioxide in Alkali Hydrog Carbonates in the Presence of Carbonates. WILHE HARTMANN (*Zeitsch. anal. Chem.*, 1920, **59**, 289—297).—When mixture of sodium hydrogen carbonate and sodium carbonate mixed with 70% glycerol solution (7 c.c. for each 0·1 gram carbonate) and heated at 115° for ten minutes, the whole of t carbon dioxide in the hydrogen carbonate is liberated, and, aft being passed through suitable drying apparatus, may be collect in an ordinary potash bulb and weighed. At the end of the t minutes the temperature should be lowered to 100°, and a curre of air passed through the apparatus to convey the carbon dioxi into the potash bulb. If the same mixture is then heated at 19 for five minutes, two drops of water now added, and the heati continued for a further ten minutes, the carbonate is decompose and the resulting carbon dioxide may be collected and weighe In most cases, the greater part of the water evolved with t carbon dioxide may be separated by means of a short refl apparatus, but when ammonium salts are present, a vessel cc taining sulphuric acid must be used for drying the gas a removing the ammonia. W. P. S.

The Conductometric Estimation of Carbonic Acid an its Salts. I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, **11** 155—164).—Solutions of carbonic acid, from 0·0015 to 0·02 m in strength, can be titrated conductometrically with alkali. T conductivity straight-line curve becomes steeper after the for ation of the hydrogen carbonate, and again steeper after t formation of the normal carbonate. The breaks in the cur however, are not sharp, especially in very dilute solutions, which, owing to the considerable hydrolysis of the carbonate, t

straight-line portions become rounded into a continuous curve. The sharpness of the titration can be greatly increased by having present an excess of calcium salt (calcium chloride) to precipitate the carbonate as it is formed. Time must be allowed during the titration for the precipitation of the calcium carbonate.

Carbonic acid cannot be titrated with carbonate to the hydrogen carbonate conductometrically, because the angle between the two portions of the curve is too obtuse. On the other hand, carbonate can be titrated with acid. According to the dilution, the conductivity may fall (in dilute solution) or rise (in stronger solutions, above $0 \cdot 1N$) up to the hydrogen carbonate point. From this point, which is not sharp, to the neutral point, the conductivity increases gradually, and at the neutral point there is a sharp rise. The neutral point is very sharp in extremely dilute solutions. Free alkali hydroxide can be estimated in presence of carbonate by titration with acid if not present in too small an amount. The amount of hydrogen carbonate in carbonate can be determined by titration with alkali or acid, but its amount must not be too small, or the direction of the corresponding portion of the curve cannot be determined with sufficient accuracy. A very weak acid, such as boric acid, can be titrated in presence of sodium carbonate with alkali hydroxide with satisfactory results. E. H. R.

Microchemical Reactions of Radium; its Differentiation from Barium by Iodic Acid. G. DENIGÈS (*Compt. rend.*, 1920, **171**, 633—635).—Radium salts give results identical with those of barium salts in the microchemical tests where hydrofluosilicic acid, oxalic acid, tartaric acid, potassium ferrocyanide, potassium tartrate, ammonium cyanurate, or ammonium phosphomolybdate in ammoniacal solution are used respectively as reagents. Iodic acid can be used, however, under certain conditions to differentiate between the salts of these two metals. If the concentration of the solution does not exceed 0·3%, radium and barium salts give typical and distinct microcrystalline precipitates with a 10% solution of iodic acid. W. G.

Titrations with Surface-active Substances as Indicators. II. Estimation of Acidity with Capillary-active Substances of Alkaline Nature. WILHELM WINDISCH and WALTHER DIETRICH (*Biochem. Zeitsch.*, 1919, **100**, 130—147. Compare this vol., ii, 48).—Salts of substances of an alkaline nature, such as quinine hydrochloride, veratrine hydrochloride, eucupine dihydrochloride, were used as indicators in acidimetric titrations, according to Traube's method, by changing the surface tension of the indicator. Eucupine dihydrochloride was found to be as sensitive as decoic acid is in alkalimetry. With this indicator, it is possible to carry out graduated titrations of a strongly dissociated acid in the presence of a primary phosphate in varying proportions. By this method, the amphoteric reaction of mixtures of primary and secondary phosphates can also be demonstrated. S. S. Z.

Titrations with Surface-active Substances as Indicators. III. Investigation of Carbonates and Phosphate–Carbonate Mixtures by Utilising Surface-active Indicators of Acid and Alkaline Nature. WILHELM WINDISCH and WALTHER DIETRICH (*Biochem. Zeitsch.*, 1919, **101**, 82—109. Compare this vol., ii, 48, and preceding abstract).—The carbonates and hydrogen carbonates of potassium and sodium react alkaline with eucupine dihydrochloride as a surface tension indicator; those of magnesium react less alkaline than the above, but more alkaline than calcium normal and hydrogen carbonates. When these carbonates are mixed with primary potassium phosphate in the cold, the two substances react until a certain equilibrium is attained, showing the same order of alkalinity as the above. This is obtained with the alkaline surface tension indicator, eucupine dihydrochloride, as well as with the acid surface tension indicator, sodium undecoate. When heated, the alkali carbonates have the same influence on the primary phosphate as alkali hydroxide. The action of magnesium and calcium hydrogen carbonates on the primary phosphate under these conditions is complicated. The alkaline action of the alkaline earth hydrogen carbonates is proportionately greater when small quantities are used than when larger ones are employed.

S. S. Z.

Estimation of Potassium as Perchlorate, and the Separation from Sodium, etc. R. LEITCH MORRIS (*Analyst*, 1920, **45**, 349—368).—A critical examination of the perchlorate method for the estimation of potassium, together with suggestions as to the most suitable forms of apparatus. The potassium salt solution should be evaporated three times with perchloric acid, and in the final evaporation taken practically to dryness. The residue is treated with 10 c.c. of wash liquid (100 c.c. of 98% by vol. alcohol and 1 c.c. of 20% perchloric acid), stirred occasionally for fifteen minutes when sodium is present, and the liquid then decanted through a weighed Gooch crucible containing asbestos. When only potassium is present, the precipitate is rinsed directly on to the filter with a small, measured quantity of the wash liquid. If sodium is present, the basin containing the precipitate from the first decantation is heated slightly to evaporate the alcohol, the precipitate dissolved in a small quantity of water, the solution evaporated to dryness, the precipitate treated with 10 c.c. of wash liquid, the latter decanted on to the filter, and the precipitate transferred by using 10 c.c. of the filtrate. Finally, the precipitate is washed on the filter by a measured volume of wash liquid, the crucible and its contents dried at 130° to 150° for one hour, cooled in a desiccator for one hour, and weighed. The weight is taken as being constant when, on washing with 3 c.c. of liquid, the difference between successive weighings does not exceed 0·2 mg. When much phosphoric acid is present, the evaporation with perchloric acid should not be to dryness, but to a moist, pasty condition; the residue is then treated with 15 c.c. of 98% alcohol, and finally washed with the wash liquid. Calcium, iron,

aluminium, and barium do not interfere, and magnesium is also without effect provided that the evaporation with perchloric acid is not carried to dryness. Organic acids tend to char during the evaporation, and when they are present it would seem preferable to separate the potassium previously by the cobaltinitrite method. In the case of sulphates, the sulphuric acid should be removed by treatment with barium chloride, but it is not necessary to remove the slight excess of barium chloride used. W. P. S.

The Precipitation of the Calcium Group and Magnesium. I. M. Kolthoff (*Pharm. Weekblad*, 1920, **57**, 1229—1234).—The sensitiveness of ammonium carbonate, as usually used for the precipitation of Group IV in presence of ammonium chloride, leaves much to be desired. Ammonium carbonate in the cold gives no precipitate with solutions containing less than 25 mg. of calcium per litre, and at that concentration the precipitate is visible only after fifteen minutes. The sensitiveness is greater at the boiling point; in presence of free ammonia, a concentration of 5 mg. of calcium per litre, shows a precipitate in boiling ammoniacal solution. Ammonium chloride renders the reaction much less sensitive. The same conclusions are found to hold for strontium and barium, the latter being least sensitive to ammonium carbonate, as would be expected from the solubilities of the Group IV metal carbonates.

Sodium carbonate is found to be a much more sensitive reagent, giving precipitates at the boiling point from solutions containing only 1 mg. of calcium, 3 mg. of strontium, or 5 mg. of barium per litre. The use of sodium hydroxide and carbonate together is recommended to ensure complete precipitation of magnesium, which can be removed by the chromate method and reprecipitated with ammonium phosphate. Considerable excess of these reagents is not harmful to the reaction, as the ammonia set free from the ammonium chloride present has no tendency to prevent precipitation of the magnesium. S. I. L.

Estimation of Calcium and Magnesium in Different Saline Solutions. E. Canals (*Compt. rend.*, 1920, **171**, 516—518).—If to a solution containing calcium, magnesium, iron, and aluminium salts, just acidified with sulphuric acid, sodium phosphate is added and the solution made alkaline with ammonium hydroxide, it is possible to retain the whole of the calcium and magnesium in solution by acidifying with acetic acid and shaking vigorously for several minutes. W. G.

Detection of Magnesium. Fritz Eisenlohr (*Ber.*, 1920, **53**, [*B*], 1476—1477).—Five c.c. of a solution of alkannin in alcohol (96%) are treated with a drop of $2N$-ammonium carbonate solution, which does not cause any change in colour, and then with a drop of the neutral salt solution; the presence of magnesium, strontium, or manganese is denoted by the development of a bluish-violet coloration which becomes pale red after acidification with one or at most two drops of $2N$-hydrochloric acid; subsequent addition of the

same number of drops of $2N$-ammonium carbonate solution restores the bluish-violet colour only if magnesium is present. If the latter is present as magnesium ammonium phosphate, the salt is dissolved in $2N$-hydrochloric acid, and a drop of this solution is added to the alkannin tincture; further addition of 1—2 drops of ammonium carbouate causes the appearance of the bluish-violet colour if magnesium is actually present, whilst otherwise the original colour of the tincture is restored. It is essential that the alcoholic solution should not become diluted with water, since in this case the ammonia hydrolytically produced gives a blue coloration. H. W.

The Acidimetric Estimation of Heavy Metals in their Salts. I. M. Kolthoff (*Zeitsch. anorg. Chem.*, 1920, **112**, 172—186).—Experiments were made to determine with what degree of accuracy the salts of heavy metals which form insoluble hydroxides can be titrated with alkali hydroxides, either by the conductometric method or with the help of indicators. The statement of Harned (A., 1917, ii, 272) that magnesium sulphate can be estimated conductometrically by titration with barium hydroxide was confirmed. Satisfactory results were also obtained by precipitating the magnesium hydroxide with excess of standard alkali, filtering, and titrating back with standard acid. The conductometric method gave unsatisfactory results when zinc sulphate was titrated with sodium or barium hydroxide, owing to the precipitation of basic salt. Better results were obtained by titrating sodium hydroxide with zinc sulphate. In the case of copper sulphate also, the formation of basic salt interferes with the titration, and satisfactory results could not be obtained. Mercuric chloride can be titrated conductometrically with accuracy by running the solution into sodium hydroxide solution, which should not be stronger than $0{\cdot}01N$. In the case of aluminium salts, when these are titrated with sodium or barium hydroxide, a sharp break in the conductivity curve is not obtained at the neutral point, but there is a very sharp break at the point where the formation of aluminate is complete. Aluminium hydroxide behaves, therefore, as a mono-basic acid. Aluminium sulphate or alum can be titrated with sodium hydroxide at the boiling temperature in presence of excess of barium nitrate, using phenolphthalein as indicator. Slight excess of alkali is run in and titrated back with acid. The results are accurate.

E. H. R.

Use of Diphenyl Derivatives in Qualitative Analysis. F. Feigl (*Chem. Zeit.*, 1920, **44**, 689—690).—Benzidine and other diphenyl derivatives yield intense blue colorations with manganic, ceric, cobaltic, and thallic compounds. For the detection of traces of the latter their solution is rendered alkaline with sodium hydroxide solution prepared with ordinary tap water (the presence of calcium carbonate is advantageous since it occludes the traces of metallic hydroxides), the mixture filtered, and the filter then treated with a drop of benzidine acetate solution. The test will detect the presence of 1 part of manganese in 125 million parts of

solution. Thallic compounds even give a blue coloration with the reagent without previous treatment with alkali; cobalt salts must be heated with alkali solution to obtain the pink hydroxide before the reaction with benzidine can be obtained. In the case of iron the blue coloration is not obtained when all the iron has been precipitated from solution by alkali. W. P. S.

Electro-analytical Separation of Nickel (Cobalt) from Arsenic. N. Howell Furman (*J. Amer. Chem. Soc.*, 1920, **42**, 1789—1793).—Nickel may be quantitatively separated from salts of arsenic acid in ammoniacal solution by the electric current. Cobalt on deposition carries down arsenic, whereas the nickel precipitate is free from arsenic. If the two metals are deposited simultaneously, arsenic may or may not be deposited, according to the conditions. J. R. P.

Volumetric Methods for Estimating Tin. J. G. F. Druce (*Chem. News*, 1920, **121**, 173—175).—Stannous tin may be more accurately estimated by a volumetric method in an acid solution. Titration with standard iodine solution in the presence of hydrochloric acid gives satisfactory results with stannous chloride, inorganic stannochlorides, and stannochlorides of aliphatic amines, but is less suitable for aromatic amine compounds, which have a tendency to darken during the titration, and so obscure the end-point. For the titration of stannous chloride with potassium permanganate solution, the hydrochloric acid should be kept as low as possible by dissolving the salt in dilute sulphuric acid, and titrating the solution as rapidly as possible. Potassium dichromate is usually less trustworthy as a reagent for the titration. C. A. M.

Estimation of Zirconium. Melvin S. Smith and C. James (*J. Amer. Chem. Soc.*, 1920, **42**, 1764—1770).—Zirconium is precipitated by selenious acid from a boiling solutiou acidified with hydrochloric acid. The basic selenite on ignition leaves zirconia. It is shown that this method gives satisfactory results in the estimation of zirconium in a pure salt, in the separation of zirconium from aluminium and rare earths, and from iron when the amount of ferric oxide in the combined oxides of iron and zirconium does not exceed 10%. Titanium is precipitated with zirconium, and a correction must be applied in this case or the precipitation carried out in presence of excess of hydrogen peroxide, when zirconium alone is precipitated. If phosphates are present the zirconium phosphate in the ammonia precipitate is insoluble in hydrochloric acid, and must be fused with sodium carbonate, boiled with water, and the residue dissolved in hydrochloric acid and added to the main solution. A method for the analysis of zirconia ore is described. J. R. P.

Estimation of Antimony in Lead-Antimony Alloys. L. Bertiaux (*Ann. Chim. anal.*, 1920, [ii], **2**, 273—278; *Bull. Soc. chim.*, 1920, [iv], **27**, 769—771; *Chim. et Ind.*, 1920, **4**, 467—472). —The alloy is dissolved by heating with sulphuric acid and

sodium sulphate, the solution is diluted with water, hydrochloric acid, and a few drops of a 0·1% solution of Poirrier's orange, and the mixture is titrated with standardised permanganate solution until the colour is just discharged. The hydrochloric acid keeps the antimony sulphate in solution, and as soon as all the antimony has been oxidised by the permanganate the next drop of permanganate solution introduced reacts with the hydrochloric acid, liberating chlorine, which decolorises the Poirrier's orange. Bismuth, copper, tin, and arsenic do not interfere; iron is titrated together with the antimony, but its quantity may be estimated colorimetrically with thiocyanate in the solution in which the antimony has been titrated. [See, further, *J. Soc. Chem. Ind.*, 1920, 693A.] W. P. S.

Sensitive Modification of Lieben's Reaction for Iodoform. RUDOLF KUNZ (*Zeitsch. anal. Chem.*, 1920, **59**, 302—303).—For the detection of traces of alcohol by this test, 10 c.c. of the solution are treated with 2 c.c. of 10% sodium hydroxide solution, 0·15 gram of potassium iodide and 0·2 gram of potassium persulphate, and the mixture is heated at 60°. A solution containing one drop of alcohol in 100 c.c. of water yields a turbidity, due to the formation of iodoform, within ten minutes. W. P. S.

The Conductometric Titration of Phenols. I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, **112**, 187—195).—Phenol and the cresols can be accurately titrated conductometrically with alkali in 0·1 or 0·01*N*-solution. Vanillin and sodium phenolsulphonate can be similarly titrated. In salicylic acid the hydroxyl group loses its acidic character and cannot be titrated, but its esters, for example, salol or methyl salicylate, can be accurately titrated as phenols; *p*-hydroxybenzoic acid behaves as a dibasic acid. Thymol and β-naphthol are also satisfactorily titrated. Of the dihydroxybenzenes, catechol behaves as a monobasic acid, the conductivity curve showing only one break, corresponding with the first hydroxyl group; quinol behaves as a dibasic acid, the first break not being very distinct, whilst resorcinol, which also behaves as a dibasic acid, gives better results when titrated with barium instead of sodium hydroxide. Pyrogallol functions as a dibasic acid, not monobasic, as stated by Thiel and Roemer (A., 1908, i, 787, 791), and so does phloroglucinol, whilst gallic acid, having a carboxyl in addition to three hydroxyl groups, behaves as a tribasic acid. E. H. R.

Estimation of Terpin. OBDULIO FERNÁNDEZ and N. LUENGO (*Anal. Fis. Quim.*, 1920, **18**, 158—165).—When terpin is treated with acetic anhydride and anhydrous sodium acetate, only one of its two hydroxyl groups is acetylated; hence it behaves like a monohydric alcohol, although the results are slightly high. When a small quantity of sulphuric acid is used instead of sodium acetate, the reaction takes place spontaneously, and one hydroxyl group is acetylated. The quantity of acetic anhydride required is two to three times that of the terpin, the mixture being left for

one or two hours. Complete esterification is achieved by Boulez's method (A., 1907, ii, 306): 5 grams of terpin are dissolved in 25 grams of rectified oil of turpentine and 40 grams of acetic anhydride. Three grams of fused sodium acetate are added, and the mixture boiled for three hours. The liquid is digested for twenty minutes on the water-bath with a little water, and a saturated salt solution added; the top layer is made up to 100 c.c. with oil of turpentine and dehydrated with calcined sodium sulphate; an aliquot part of the liquid is then hydrolysed with alcoholic $N/2$-sodium hydroxide solution. W. R. S.

An Accelerated Method of Estimating the Reducing Values of Cellulosic Substances. E. KNECHT and L. THOMPSON (*J. Soc. Dyers and Col.*, 1920, **36**, 255—257).—Schwalbe's method for estimating the copper number of oxycellulose is modified by adding the cuprous oxide to a ferric salt solution and titrating the ferrous salt so formed with potassium permanganate. By this means it is unnecessary to determine the unreduced copper absorbed by the cellulose (copper hydroxide number), which is the difference between the above number and that obtained from an estimation of the unreduced copper in the filtrate by titanous chloride.

The copper number may be determined by a process based on the fact that oxycellulose precipitates cuprous thiocyanate from solutions of the cupric salt. This method avoids the errors that the action of the alkali hydroxide in Fehling's solution on oxycellulose may cause.

The copper number may also be determined by heating oxycellulose with sodium hydroxide and rosinduline, and then titrating with titanous chloride to determine the amount of dye reduced.

All three methods give sufficiently accurate results, and are more quickly carried out than the original Schwalbe method. [See *J. Soc. Chem. Ind.*, 1920, 718A.] A. J. H.

Estimation of Acetic Anhydride. KNUT WOLOAST (*Svensk Kem. Tidskrift*, 1920, **32**, 110).—Twenty-five c.c. of acetic anhydride are dissolved in 30 c.c. of benzene, 25 c.c. of water are added, and after vigorously shaking for fifteen seconds the aqueous layer is drawn off and measured. The increase in volume is due to the acetic acid present, and multiplied by 4 gives the percentage of acetic acid. Some small amount of acetic anhydride will dissolve in water and some of the dilute acetic acid will dissolve in the benzene. A table of corrections is necessary In the following pairs of figures the first is the burette reading of increased volume multiplied by 4 and the second the corrected percentage: 93·5—100, 90—95·6, 85—89·6, 80—81·5, 75—75·8, 55—55·1, 50—50·1, 35—33·3, 25—21·7, 20—15·5, 11—0. CHEMICAL ABSTRACTS.

Colour Test for Oxalic Acid. LEWIS H. CHERNOFF (*J. Amer. Chem. Soc.*, 1920, **42**, 1784—1785).—A few crystals of resorcinol are dissolved in 5 c.c. of the solution by warming gently. The

liquid is cooled and an equal volume of concentrated sulphuric acid slowly poured in to form a layer. A blue ring is formed at the junction of the layers if oxalic acid is present. If the blue colour does not appear, the liquids are mixed by shaking, and, after cooling somewhat, another 5 c.c. of sulphuric acid added. If the colour still fails to appear, the liquid is warmed over a flame (not boiled), when an indigo-blue colour appears. If the mixture is boiled the colour becomes dark green. J. R. P.

Detection of Coumarin in Vanillin. L. GERET (*Mitt. Lebensm Hyg.*, 1920, **11**, 69—71).—Five % of coumarin in vanillin can be detected by the yellow turbidity produced by the addition of a 1% solution of iodine in 2% potassium iodide solution; the turbidity changes to lustrous, metallic, bluish-black crystals containing 46·47% of iodine and yielding 13·36% of ash.

CHEMICAL ABSTRACTS.

Estimation of Aminoethyl Alcohol and of Choline appearing on the Hydrolysis of Phosphatides. P. A. LEVENE and T. INGVALDSEN (*J. Biol. Chem.*, 1920, **43**, 355—378).—The method is a modification of that introduced by Thierfelder and Schulze (A., 1916, i, 548). This method is employed in the original form up to the point where the free aminoethyl alcohol is extracted. This is accomplished by boiling the mixture of the hydrochlorides of the two bases and an excess of calcium oxide with dry acetone. The combined acetone extracts are acidified with hydrochloric acid, and evaporated in a vacuum. The residue is dissolved in water, evaporated to a syrup, and again treated with calcium hydroxide and acetone. The final acetone extracts are filtered, made acid with hydrochloric acid, and the acetone removed by vacuum evaporation.

The residue from the acetone extracts is treated with water and filtered from calcium hydroxide. Hydrochloric acid and the residual calcium are removed by silver oxide and carbon dioxide respectively. The choline is precipitated as picrate.

In an actual experiment on the separation of the bases from the ether-soluble, acetone-insoluble lipoids from egg, 77·5% of the amino-nitrogen was found present in the acetone extracts, whilst the yield of choline was 98·7% of the theory. J. C. D.

Separation and Estimation of Phenylalanine. SHINTARO KODAMA (*J. Tokyo Chem. Soc.*, 1920, **41**, 479—495).—In the ester or the lime method glutamic acid, aspartic acid, and phenylalanine are collected in the same fraction. The author adds lime to the mixture of the products of hydrolysis of a protein, whereby basic calcium glutamate is precipitated. The calcium salts subsequently obtained by concentrating the filtrate are washed with water or lime-water, heated with 7 to 8 volumes of water, and treated with carbon dioxide, whereby calcium carbonate is precipitated. When this filtrate is concentrated, phenylalanine crystallises.

An approximate estimation of the phenylalanine in a mixture of the calcium salts of phenylalanine (Ca, 9·98; H_2O, 8·91%), glutamic

acid (Ca, 16·80; H_2O, 22·56%), and aspartic acid (Ca, 16·51; H_2O, 29·63%) can be made if the percentage of calcium and of water of crystallisation is estimated. By suspending the mixture in hot water and treatment with carbon dioxide, calcium glutamate and aspartate lose one-half of their calcium, and are converted into easily soluble, normal calcium salts, whilst the calcium salt of phenylalanine loses the whole of its calcium, and is converted into the free acid. The difference between the amount of calcium in the precipitate and in the solution corresponds with the amount of calcium originally combined with phenylalanine.

Several methods of obtaining perfumes from phenylalanine are described. CHEMICAL ABSTRACTS.

Estimation of Taurine in Muscle. Y. OKUDA and KEIICHI SANADA (*J. Coll. Agr. Imp. Univ. Tokyo*, 1919, **7**, 77—80).—Sulphur is estimated in an aqueous extract of the muscle, after removal of all compounds of sulphur except taurine, for example, proteins, sulphates, and cystine (if necessary). The flesh (5 grams if fresh, 1 gram if dry) is ground and extracted first with cold water, then with warm water. The total extract is boiled with the addition of acetic acid; the coagulum is removed; the filtrate is neutralised, and is precipitated with basic lead acetate, an excess of that reagent being avoided. The precipitate is removed by filtration; the filtrate is treated with sulphuric acid to precipitate the excess of lead; excess of sulphuric acid is removed with baryta, and excess of baryta with ammonium carbonate. The final filtrate is used for the estimation of sulphur, which is converted into sulphate and weighed as barium sulphate. Multiplication of the weight of barium sulphate by the factor 0·5358 gives the weight of taurine. Cystine is usually absent from the extract; if it is present, the above technique is modified; after precipitation of the excess of lead, more sulphuric acid is added until its concentration reaches 5%; the cystine is then precipitated with phosphotungstic acid and removed by filtration after remaining for two or three days. Treatment with baryta and with ammonium carbonate and estimation of taurine sulphur are made as usual. The percentage of taurine in fresh flesh and, in parentheses, in dry flesh, was: shark, 0·13 (0·61), carp, 0·13 (0·61); ordinary flesh of bonito, 0·08 (0·30); "chiai" flesh of bonito, 0·42 (1·56); *Neptunus pelagicus*, 0·28 (1·37), *Palinurus vulgaris*, 0·17 (0·76); *Pinna japonica* (adductor muscle), 0·54 (2·38); *Avicula martensii* (mantle), 0·91 (5·20). All the samples of muscle (fish, mollusc, and crustacean) examined contained taurine; that compound was most abundant in molluscs, and less abundant in fish, although present in comparatively large amount in their "chiai" flesh. CHEMICAL ABSTRACTS.

Detection of Cyanic Acid. R. FOSSE (*Compt. rend.*, 1920, **171**, 635—637).—The cyanic acid may be detected directly as such or after its conversion into silver cyanate. In the first case portion of the solution is heated for one hour with ammonium chloride, and the carbamide present in 2 c.c. of the solution th

eated and in 2 c.c. of the untreated solution is estimated by leans of xanthhydrol. An increase in the carbamide content of the olution by heating with ammonium chloride is evidence of the resence of cyanic acid. In the second case the silver cyanate is eated with ammonium chloride, and the resulting liquid tested for arbamide as above. Another portion of the silver cyanate is first eated with nitric acid and then with ammonium chloride, but in his case there is no formation of carbamide. W. G.

Volumetric Estimation of Thiocyanate by Potassium ermanganate. R. Meurice (*Ann. Chim. anal.*, 1920, [ii], **2**, 72—273).—Trustworthy results are obtained when the thiocyanate olution is acidified with sulphuric acid, treated with an excess of andardised potassium permanganate solution, and the excess of le latter then titrated with dilute hydrogen peroxide solution. he excess of permanganate added should be at least one-half of lat required for the oxidation of the thiocyanate. Direct titration thiocyanate in acid solution with permanganate yields low sults. W. P. S.

Detection of Hydrogen Cyanide. James Moir (*J. S. African ssoc. Anal. Chem.*, 1920, **3**, 16. Compare P., 1910, **26**, 115).—ilter paper is moistened with a reagent consisting of *o*-tolidine gram, copper acetate 1·5 grams, glacial acetic acid 0·5 gram, id water 100 c.c., and is then suspended in the atmosphere to tested A blue colour appears on the paper if the air contains little as 1 part of hydrogen cyanide in 2 millions. W. P. S.

Preparation of Phosphomolybdic Acid and its Applicaon to the Colorimetric Estimation of Uric Acid. . Proschowsky (*Kongl. Vet. Landbohöjskole Aarskrift*, 1918, '2—407; from *Chem. Zentr.*, 1920, iv, 315).—The author reviews e colorimetric methods which have been proposed for the estimaon of uric acid in urine, and indicates a new procedure for the eparation of phosphomolybdic acid required in Höst's process; e latter has been examined in detail, and certain improvements e recommended. H. W.

Nuclein Metabolism. IX. Detection and Estimation of ombined and Free Purines in Human Blood and Pus erum. S. I. Thannhauser and G. Czoniczer (*Zeitsch. physiol. hem.*, 1920, **110**, 307—320. Compare A., 1919, i, 228).—For the timation of the free purines in blood the serum is diluted with ater and precipitated with 1·55% uranium acetate. The filtrate boiled with some sodium acetate and sodium hydrogen sulphite id precipitated with 10% copper sulphate. The precipitate is ntrifuged, washed, and the nitrogen in it is determined by the icro-Kjeldahl method. From the value obtained, the free purine ntent is calculated. The figures of the uric acid content of serum tained by the colorimetric method and by the above method ree fairly well, and it is therefore to be concluded that only very

small quantities of free purines other than uric acid are present in the blood. In order to estimate the combined purines (nucleotides) in the blood, the diluted serum is boiled, and precipitated with a 20% solution of sulphosalicylic acid in order to remove the proteins. The filtrate is concentrated and the purines are precipitated with copper sulphate as previously described, and the total purines are obtained from the nitrogen estimation, whilst the combined purines are calculated by difference. One hundred c.c. of *normal human serum contain 2—3 mg. of nucleotide nitrogen* and 1—1·5 mg. of free purine nitrogen. S. S. Z.

Colorimetric Estimation of Adrenaline. WILBUR L. SCOVILLE (*J. Ind. Eng. Chem.*, 1920, **12**, 769—771).—A mixture of 20 c.c. of water, 5 c.c. of 1% potassium iodate solution, and 0·25 c.c. of *N*/1-hydrochloric acid is heated at 38°, and 0·5 c.c. of a 0·1% solution of the sample is added. A similar mixture is prepared, but using 0·5 c.c. of pure adrenaline solution. Both mixtures are kept at 38° for fifteen minutes, then cooled, and the colorations compared. If the coloration of the test solution differs by more than 25% from that of the standard, the estimation should be repeated, using more or less of the solution. The pure adrenaline solution is prepared by dissolving 0·5 gram of the substance in 0·5 c.c. of *N*/1-hydrochloric acid and diluting the solution to 50 c.c.; if the solution to be examined contains sodium hydrogen sulphite, 0·05 gram of the latter should be added to the standard solution. W. P. S.

Important Source of Error in the Examination of Urine for Albumin with Sulphosalicylic Acid. GRETE LASCH and JOSEF REITSTOETTER (*Münch. med. Woch.*, 1920, **67**, 484—485; from *Chem. Zentr.*, 1920, iv, 30).—Schall's assumption (this vol. ii, 398) that sulphosalicylic acid forms a precipitate with calcium chloride which can be mistaken for a precipitation of albumin is untenable. H. W.

Detection of Slight Traces of Hæmoglobin in Urine. J. PITICARIU (*Compt. rend. Soc. Biol.*, 1920, **83**, 605—607; from *Chem. Zentr.*, 1920, iv, 31).—Spectroscopic examination of perfectly fresh urines which contain traces of hæmoglobin and to which Ehrlich's reagent (dimethylaminobenzaldehyde + hydrochloric acid) has been added, shows the characteristic absorption bands of oxyhæmoglobin at dilutions at which this is otherwise not the case. H. W.

[Quantitative Comparison of] Vitamine Content. WALTER H. EDDY and HELEN C. STEVENSON (*J. Biol. Chem.*, 1920, **43**, 295—309).—The methods proposed by Bachmann (A., 1919, i, 613) and by Williams (A., 1919, i, 463) have been used for quantitative studies on the vitamine-*B*. A new technique is described which eliminates some of the difficulties in the manipulation of these two tests. It is shown that this method may be utilised in estimating the vitamine content of food. J. C. D.

General and Physical Chemistry.

Atomic Refraction. W. SWIENTOSLAWSKI (*J. Amer. Chem. Soc.*, 1920, **42**, 1945—1951).—*A theoretical paper in which it is shown* that the atomic refractions of carbon and hydrogen in hydrocarbons vary with the constitution of the hydrocarbon. The molecular refraction, M_D, of a hydrocarbon C_nH_m may be expressed by the equation $M_D = nr_{CH_2} + (m-2n)r_H + \Sigma\Delta r_C + \Sigma\Delta r_H$, in which r_C, r_H and r_{CH_2} are the refractivities of carbon, hydrogen, and the group CH_2 respectively. The individual refractivities may be evaluated from this equation when $\Sigma\Delta r = \Sigma\Delta r_C + \Sigma\Delta r_H$ is assumed equal to zero. Making use of the known molecular refractivities of eight hydrocarbons, the values $r_C = 2{\cdot}490$, $r_H = 1{\cdot}066$, and $r_{CH} = 4{\cdot}622$ are obtained as mean values. These values differ in two cases from Eisenlohr's values, $r_C = 2{\cdot}418$, $r_H = 1{\cdot}100$, and $r_{CH_2} = 4{\cdot}618$ (*A.*, 1911, ii, 81). The value for CH_2 is in agreement, whilst the other values differ by ±3%. This divergence is explained by the fact that the value for M_D comes from two factors, $M_D = nr_{CH_2} + \Sigma r_x$, of which the former is large, and consequently small errors cannot affect M_D to a marked extent. In the case of alcohols, the value $r_O = 1{\cdot}494$, which is 2·03% smaller than Eisenlohr's value; for ethers $r_O = 1{\cdot}663$, whilst Eisenlohr's value is 1·643, or 1·2% less. *It is stated that the calculation of average values for atomic* refraction is insufficient for practical purposes, and the change of the value with constitution must be taken into account.

J. F. S.

The Molecular Refraction Coefficient, its Additivity and its Use for Determining Constitution. FRITZ EISENLOHR and EDGAR WÖHLISCH (*Ber.*, 1920, **53**, [*B*], 1746—1766).—The molecular refraction calculated from the expression $fn \,.\, M/d$, where $fn = n^2 - 1/n^2 + 2$, is not very sensitive to constitutive influences, and is unsuitable as a constant for determining the purity of a substance because, *in the case of an impure substance*, the refractive index and density may have a mutually compensating effect. It is claimed that the expression $M \times n$, termed the molecular refraction coefficient, is in many respects superior. This quantity has been calculated for a large number of organic compounds, using n_D^{20}, and has been found to be very sensitive to constitutive influences. In the paraffins, primary alcohols, aldehydes, ketones, acids and esters, the mean value of $M \times n_D^{20}$ for CH_2 is 20·56, for C, 25·55; H, −4·99. The values for oxygen are, in hydroxyl, 26·54; in ethers, 22·97; in aldehydes, 17·40; in ketones, 16·98. For the ethylenic double bond, −6·17 is found. It is to be noted that the influence of a double bond, whether between two carbon atoms or between carbon and oxygen, is negative, instead of positive as in the old molecular refraction. The probable error

in the above figures is 0·2 unit. The influence of a side-chain in the paraffin series varies with the position of the tertiary carbon atom. If the side-chain is attached to the second carbon atom, its effect is equal to $-0·2$ unit, but on the third or fourth carbon atom its sign is reversed, and it amounts to 0·45.

In cyclic, non-aromatic compounds, the effect of ring formation is more marked on the new molecular refraction-coefficient than on the old. The values found were $-5·5$, $-4·9$, $-4·2$, $-3·4$, $-2·2$, and $-1·1$ for the three- to eight-membered rings respectively. The entry of a side-chain into the six-ring system has a further lowering effect on the coefficient, and in the disubstituted compounds this negative effect is magnified, most in the para- and least in the ortho-compounds. The double bond in the polymethylenes has the same value as in the open-chain compounds, but in the substituted polymethylenes its influence depends on its position in relation to the side-chains.

In aromatic compounds, the allowance to be made is not equivalent to a six-membered ring with three double bonds, but the total effect is equal to $-21·2$ units. In contradistinction to the polymethylenes, the effect of substituents in the benzene series is positive. Certain numerical relationships appear to exist between the effects of substitution in the aromatic and polymethylene series respectively.

In the series of aliphatic acids and esters, certain optical abnormalities appear, which can be explained on the assumption that a loose, four-membered ring is present in the structure of the type

$$\begin{array}{l} R\cdot C{=}O \\ \;\;\;\;| \quad\;\; \vdots \\ \;\;\;\;O{-}CH_2\cdot R \end{array}$$

E. H. R.

Mass Spectra of Chemical Elements. II. F. W. Aston (*Phil. Mag.*, 1920, [vi], **40**, 628—634. Compare this vol., ii, 344). —The mass spectra of boron, fluorine, silicon, bromine, sulphur, arsenic, and phosphorus have been measured by the method previously described (*loc. cit.*). The results show that all seven elements obey the whole-number rule within the accuracy of the experiment. Of the elements examined, boron, silicon, and bromine are definitely complex; they are composed of two isotopes, in each case of the following relative masses: boron, 11, 10; silicon, 28, 29, (30); bromine, 79, 81; the masses are given in order of intensity, and the parenthesised number indicates a douhtful mass. In the case of bromine, two lines are obtained, corresponding with masses of 80 and 82; these correspond with hydrogen bromide from the two bromine isotopes; similarly, lines of two boron difluorides have been identified. Some anomalous fractional lines are mentioned and their possible origin discussed. J. F. S.

Spectrum of Neon. F. Paschen (*Ann. Physik*, 1920, [iv], **63**, 201—220. Compare this vol., ii, 69).—A theoretical paper in which the series occurring in the spectrum of neon are discussed. The neon spectrum is composed of ten sequences of the principal

series type and fourteen sequences of the subsidiary series type. The limits of the series which result by the combination of one set of sequences show a constant difference in wave-length of 782 cm.$^{-1}$ when compared with the combinations from the associated set, independent of the type of the series. This modification of the combination principle results when the limits of all series are calculated according to the Ritz formula. J. F. S.

Comparison between the Spark Spectra of the Alkaline Earths and the Arc Spectra of the Alkalis. ERWIN FUES (*Ann. Physik*, 1920, [iv], **63**, 1—27).—A theoretical paper in which arc spectra of the alkalis and the spark spectra of the alkaline earths are considered with the object of examining Sommerfeld and Kossel's second hypothesis, the displacement hypothesis, which states that an element in its spectral behaviour is displaced to that of the element occupying the preceding position in the periodic system when an electron is removed from its outer sheath by ionisation, that is, when it is brought into such a condition that it can emit its spark spectrum. The result of the theoretical consideration is to confirm the hypothesis. As an addendum to the paper, the doublet series are given in tables for magnesium, calcium, strontium, and barium, as well as the second subsidiary series of single lines for zinc, cadmium, and zinc, and the first subsidiary series of aluminium. J. F. S.

Spark Spectra of some Elements in the Extreme Ultra-violet. LÉON BLOCH and EUGÈNE BLOCH (*Compt. rend.*, 1920, **171**, 709—711).—A study of the spark spectra of antimony, arsenic, bismuth, and tin over the range $\lambda = 1850$—1400.

In this region, antimony shows a number of sharp, intense lines. The spectrum of arsenic is composed of weak and often diffused rays. The two characteristic intense lines of arsenic in this region are $\lambda = 1805{\cdot}6$ and $\lambda = 1660{\cdot}8$. Four new rays of tin, $\lambda = 1655{\cdot}3$, 1656·9, 1574·6, and 1570·6, respectively, were obtained. The complete spectrum of bismuth between $\lambda = 1823$ and 1390 is given.
W. G.

Effect of a Magnetic Field on the Intensity of Spectrum Lines. H. P. WARAN (*Proc. Camb. Phil. Soc.*, 1920, **20**, 45—49). When a small portion of the capillary of a mercury discharge tube was subjected to a magnetic field of about 5000 *C.G.S.* units, the light was found to change in colour and intensity opposite the pole pieces. The tube originally gave the principal mercury lines 5790·66, 5769·6, 5460·7, 4916·0, and 4358·34, and the hydrogen lines 6563, 4861·5, and 4340·7; on applying the magnetic field, new lines at 5426, 5679, 5872, and 5889, as well as a very strong red line at 6152, appeared. Exhausting the tube still further and increasing the current to 5 milliamperes produced four faint lines at 6234, 6152, 6123, and 6072; the effect of the field on these lines is to increase the intensity of 6152 about five times, whilst the others, if they change at all, suffer a decrease in intensity. In

a hydrogen tube containing a trace of mercury, the helium lines are intensified, whilst hydrogen lines are practically unaffected, or even slightly reduced in intensity. In a neon tube containing a trace of hydrogen, the neon lines were considerably enhanced. *The experiments indicate that in a mixture of monatomic and diatomic gases, the monatomic gases alone seem to be affected in a peculiar way, resulting in their spectrum lines alone being very considerably enhanced or brought out prominently,* even when not visible at all previously. In the case of atmospheric air, the effect of *the field is to bring out new lines* which are not present without the field, and although one or two of these lines have the same wave-lengths as previously catalogued lines of oxygen or nitrogen, many of them have not been identified. J. F. S.

Centres of Absorption of Coloured Solutions. Emilio Adinolfi (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 38—41).—In view of the disadvantages attending the usual methods employed to ascertain *the centres* of the bands of absorption spectra, the author suggests the following procedure, which gives continuous absorption curves. The *light*, before *impinging* on the *slit of the* spectrograph, is passed through concentrations of the substance, *diminishing regularly by diffusion*. By *means* of *a capillary* funnel, the solution is passed to the bottom of a test-tube containing the *solvent*, the *tube serving* as a *lens*. The *surface* of separation between solvent and solution being arranged normally to the slit, the field of the spectrograph shows, prior to diffusion, a sharp demarcation between the part of the absorption spectra and that corresponding with the solvent alone. As diffusion begins, the centres of absorption become successively blunted in dependence on their intensity, and become distributed on a curve which is a function of the wave-length, the intensity of absorption, and the gradient of the concentration.

Photographic investigation shows that the absorption spectra of potassium and calcium permanganates exhibit eight centres of absorption, the third, with the wave-length 5255 Ångström units, having the greatest intensity. The two absorption spectra are identical within the limits of accuracy of the measurements made. The frequencies of the eight centres of the visible spectrum are connected by means of the relation $\nu=\nu_m \pm 753n$, where ν_m represents the frequency of the maximum of the centres and n the whole numbers from -2 to $+5$. T. H. P.

Absorption of Light by Elements in the State of Vapour. (Sir) J. J. Dobbie and J. J. Fox (*Proc. Roy. Soc.*, 1920, [*A*], **98**, 147—153).—The absorption of the elements selenium, tellurium, mercury, zinc, cadmium, phosphorus, arsenic, and antimony was determined. Reproductions of the spectra are given. In the case of selenium, there is an increase in the amount of absorption from 510° to about 650°, from which point it diminishes up to about 850°. These changes are accompanied by changes in colour of the

vapour. The spectrum of selenium shows many narrow and sharp absorption bands, and presents generally the same channelled character as the spectrum of sulphur (A., 1919, ii, 334). The maximum absorption corresponds with a vapour density indicating an average value of 3 atoms in the molecule. In the case of tellurium, the general absorption increases with rise of temperature up to about 1250°, after which it diminishes to about 1350°. The spectrum is channelled. At 1250°, the constitution of tellurium vapour would appear to be analogous to that of sulphur and selenium at 650°.

Zinc, cadmium, and mercury show a different behaviour. They are transparent to light as far as the spectrum of the Nernst filament extends, that is, to about 3100. Increase of temperature is *not accompanied by the peculiar behaviour exhibited by sulphur*, and (unlike the results with sulphur, selenium, and tellurium) increase in quantity of the element within the limits of the experiments has little influence on the spectrum.

Phosphorus, arsenic, and antimony show an increase of absorption with rise of temperature. It is concluded that this is closely associated with the breaking down of complex molecules. No absorption bands or indications of any kind of selective absorption were observed in the elements of this group.

The elements studied are divided into three groups: (1) Elements the vapours of which exercise no absorption or show only a few well-defined absorption bands; these are monatomic. (2) Elements in which the absorption gradually increases as the temperature is raised, but which show no other effect within the limits of temperature imposed by the method; these are tetratomic. (3) Elements in which the absorption increases with increase of temperature to a maximum, and afterwards diminishes. The sulphur and halogen elements belong to this group. The results are explained by the rearrangement of valencies accompanying the breaking down of complex molecules. J. R. P.

Influence of Dissociation on the Absorption of Potassium Permanganate. EMILIO ADINOLFI (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 87—89).—The absorption spectrum of potassium permanganate is not influenced by the extent to which the salt is dissociated. T. H. P.

The Absorption Spectrum of Europium. WILHELM PRANDTL (*Ber.*, 1920, **53**, [*B*], 1726—1728).—The absorption spectrum of europium was examined with a solution containing 20 grams of oxide as nitrate in 100 c.c., through a depth of 10 cm. A weak but characteristic, sharp, narrow line was found at λ 579. This is probably identical with the line placed by Demarçay at λ 590. It was also found that Demarçay's band at λ 465 is, in reality, a triplet, consisting of three strong, sharp lines at 465·6—465·3, 465·0—464·7, and 464·6—464·3. In other respects, Demarçay's observations were confirmed. E. H. R.

Measurement of the Luminous Intensity Diffused l Argon. New Determination of Avogadro's Constar J. Cabannes (*Compt. rend.*, 1920, **171**, 852—854).—The auth has determined the ratio, *R*, between the intensity diffused late ally by 1 c.c. of argon and the illumination of a normal plane l an incident luminous ray, the gas being illuminated by the radi tion $\lambda=4358$. The value obtained for *R* with a sample of ga containing 91% of argon, 8·7% of nitrogen, and 0·3% of oxyge was $(1{\cdot}34\pm0{\cdot}05)\times10^{-8}$/cm.

Further, the author has shown that the polarisation of the light diffused laterally by argon is almost complete, and applying the theory of Rayleigh, he finds for Avogadro's constant the value $(6{\cdot}90\pm0{\cdot}25)\times10^{23}$. W. G.

Alkaline Earth-Oxygen Phosphorescent Substances. Ferdinand Schmidt (*Ann. Physik*, 1920, [iv], **63**, 264—294).—A number of substances which become phosphorescent when subjected to light have been prepared from the oxides of calcium, strontium, and barium. These oxides were mixed, respectively, with a small quantity of one of the following substances: sodium chloride, sodium fluoride, sodium phosphate, calcium fluoride, magnesium fluoride, lithium phosphate, potassium hydrogen phosphate, and potassium borate, and thoroughly ground together; then a small measured quantity of a nitric acid solution of one of the following nitrates was added: bismuth, copper, manganese, or lead. The mixture was thoroughly mixed and heated to a red heat. These mixtures were excited by means of the light from a series of sparks between aluminium poles in water, and in this way the whole spectrum down to 220 $\mu\mu$ was obtained. The influence of different wave-lengths in exciting the phosphorescence was measured, as well as the position of the phosphorescent bands. From a comparison of the analogous oxygen, sulphur, and selenium phosphorescent substances, the following conclusions are drawn: (1) The positions of brightest phosphorescence after illumination and those of the bands are shifted to shorter wave-lengths in the oxygen compounds, and to longer wave-lengths in the selenium compounds in comparison with the sulphur compounds. This would point to the oxygen compounds having a smaller dielectric constant than the sulphur compounds, and the selenium compounds a larger dielectric constant. The bands of the oxygen compounds have a higher temperature position, and those of the selenium compounds a lower temperature position, than the sulphur bands. J. F. S.

The Existence of Intermediate States in the Phosphorescence of Calcium Sulphide deduced from the Study of its Conductivity. P. Vaillant (*Compt. rend.*, 1920, **171** 713—714).—In continuation of previous work (A., 1912, ii, 419) much larger variations in the conductivity of calcium sulphide by exposure to diffused sunlight have been obtained. The conductivity increases with the time to a maximum, and ther

decreases if the exposure is continued. The reverse occurs if the sulphide is then kept in obscurity at constant temperature, but the maximum reached in this case is much higher than during excitation. If during excitation the sulphide is removed to obscurity before the conductivity has attained its maximum, the latter continues to increase, but, however, a much lower maximum is much more rapidly reached. W. G.

Inorganic Luminescence Phenomena. I. [The Influence of] Crystalline Form, Flux, and Actual Fusion on the Phosphorescence of Zinc Sulphide. Erich Tiede and Arthur Schleede (*Ber.*, 1920, **53**, [*B*], 1721—1725).—The flux may act in one of two ways in inducing the phosphorescence of such a substance as zinc sulphide; it may either favour the appearance of a particular phosphorescent, crystalline form, or it may intermolecularly increase the pressure or lower the melting point. In the case of zinc sulphide, the two possibilities were investigated by preparing the two crystalline modifications in as pure a form as possible, and by determining the effect of actually melting the zinc sulphide by the method already described (see this vol., ii, 757). Blende (sphalerite) was found to be non-phosphorescent in the pure state, but when prepared by heating amorphous zinc sulphide with potassium chloride in the proportion 2:1 at 800° for forty-eight hours, it was phosphorescent. Wurtzite, the hexagonal form, prepared by sublimation of zinc sulphide, taking the greatest precautions against contamination, was also non-phosphorescent. On the other hand, pure fused zinc sulphide was strongly phosphorescent. It follows that there is no connexion between phosphorescence and crystalline form in the case of zinc sulphide, whilst the effect of a flux can be reproduced by fusing the pure sulphide. Fused pure alkaline earth sulphides were also found to be phosphorescent. E. H. R.

Fluorescence, Dissociation, and Ionisation in Iodine Vapour. K. T. Compton and H. D. Smyth (*Science*, 1920, **51**, 571—572).—(I) *Fluorescence and Ionisation.*—The fluorescence of gases and vapours is not generally accompanied by ionisation. Hence, the recent view has been that the primary effect of the exciting light is to cause one or more electrons to take positions or conditions of abnormally large potential energy, without being necessarily removed from the parent molecule. The authors have obtained experimental evidence of the correctness of this view from measurements of the minimum energy required to ionise a fluorescing molecule. The former requires 10 volts, the latter 7·5 volts, when excited by the green mercury line. The difference, 2·5 volts, corresponds with the quantum of energy of the frequency of the exciting light by the relation $eV = h\nu$. This offers direct evidence of the existence of molecules the electrons of which possess abnormal potential energy as a result of the exciting light. (II) *Dissociation and Ionisation.*—Two types of ionisation were discovered in iodine vapour, a very weak ionisation at 8·5 volts,

attributed to the ionisation of atoms present because of the h filament, and a very intense ionisation at 10 volts, attributed the ionisation of the molecules. The difference, 1·5 volts, cor sponds exactly with V in the relation $eV = W$, where W is the he of dissociation of iodine reckoned for a single molecule. Probab this method may be of value in determining heats of dissociati which are too high to be found by ordinary methods.

CHEMICAL ABSTRACTS.

***X*-Ray Fluorescence of certain Organic Compounds** H. S. NEWCOMER (*J. Amer. Chem. Soc.*, 1920, **42**, 1997—2007). —The author has studied the fluorescence induced in a large number of substances with the object of finding a substance which will convert *X*-rays into rays of wave-lengths which will be bactericidally active, that is, wave-lengths in the mid-ultraviolet. The fluorescence was judged as to its visibility by an eye accommodated to darkness, since it was found that in most cases the visible rays emitted were too feeble to blacken a photographic plate, and in those cases where a bright fluorescence was observed, the light was examined by a Hilger quartz spectrometer. Three inorganic salts, 308 organic compounds, apart from dyes, and 157 dyes were examined, some in solution and others in the pure condition Of all these compounds, sodium bromide alone gives a fluorescence with a wave-length lying in the required region. Many of the organic compounds fluoresce brightly in the visible region of the spectrum, and a fair number of them give fluorescence which is capable of blackening a photographic plate. The fluorescence is not limited to any physical state, and the nature of the fluorescence excited in any material, both as to intensity and quality, is independent of the quality of the exciting *X*-rays and dependent on their energy alone. It is shown, incidentally, that air becomes slightly fluorescent under the experimental conditions. The *X*-ray tubes were fed by a current of about 15 milliamperes at 10,000 to 70,000 volts.

J. F. S.

Specific Rotation of Optically Active Liquids in the Pure State and in Solution. W. DEUTSCHMANN (*Zeitsch physikal. Chem.*, 1920, **95**, 385—406).—A theoretical paper in which it is shown that the specific rotation of active substances in solution may be calculated, when the assumption is made that the specific rotation of an active substance is a constant quantity at all concentrations and in all solvents. To make this calculation, it is necessary to accept the Dolezalek theory of concentrated solutions (A., 1909, ii, 22; 1910, ii, 184; 1913, ii, 481, 482; this vol. ii, 32). Apparent divergence between observed rotation values and the calculated values are explained by the formation of active compounds between the two components of the solution, or by the presence of associated molecules of the active substance. The equations put forward are applied to the experimental results of Scheuer (A., 1910, ii, 470) for solutions of diethyl diacetyltartrate

n ethylene dibromide, and it is shown that here both disturbing actors are present. For the sake of simplicity in calculation, it s assumed that the specific rotation of the double molecules is the ame as that of the simple molecules, and the slight divergences etween the calculated values and the observed values are taken o indicate that the above assumption is not entirely justified. The very marked dependence of the specific rotation of many substances on the temperature is due to a change in the degree of association with change of temperature, and also to the fact that the double molecules have a different specific rotation from the single molecules. J. F. S.

Photochemical Decomposition of Potassium Cobaltioxalate and its Catalysis by Neutral Salts. F. M. JAEGER and G. BERGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 84–94).—The decomposition of a solution of potassium cobaltioxalate by light occurs as follows: $2Co(C_2O_4)_3''' = 2Co(C_2O_4)_2'' + C_2O_4'' + 2CO_2$ and $Co(C_2O_4)_2'' \rightleftharpoons Co^{\cdot\cdot} + 2C_2O_4''$. The reaction was studied under different conditions by Vránek (*Zeitsch. Elektrochem.*, 1917, **23**, 336). In the present experiments, a quartz mercury lamp was used as the source of light, and the reaction carried out in quartz vessels. The quantities of salt decomposed in identical intervals of time are approximately independent of the initial concentration, and are chiefly determined by the light energy absorbed. The reaction is therefore described as photocatalytic. Exact proportionality between the amount of decomposed substance and the time of exposure, with the same initial concentration, was not, however, found. This is attributed to the change of absorptive power of the solution. Exact experiments with the pure salt showed that the speed of reaction was relatively greater with the smaller than with the higher concentrations, and some disturbing influence appeared to be active. Addition of alcohol had no appreciable effect, but a strong influence on the speed of reaction was found to be exerted by neutral salts. Chlorides of potassium, sodium, lithium, magnesium and glucinum, and ferric chloride, were used. The curves exhibited a maximum of velocity with a certain concentration of each salt, and the action may pass over into a retardation. The maxima are situated at smaller concentrations as the valency of the cation is greater. Each ion has a specific effect in addition to that of its positive charge. J. R. P

New Theory of Photographic Phenomena. A. DAUVILLIER (*Compt. rend.*, 1920, **171**, 717—719).—A further development of a new theory explanatory of photographic phenomena (compare this vol., ii, 654). W. G.

Ionisation and Production of Radiation by Electron Impacts in Helium, Investigated by a New Method. K. T. COMPTON (*Phil. Mag.*, 1920, [vi], **40**, 553—568).—A method is described whereby ionisation and radiation may be distinguished

and the proportion of either estimated when both are present. The ionisation chamber is similar to that used by Franck and Hertz (A., 1913, ii, 174). A tungsten wire, 0·8 cm. long and 0·08 mm. diam., serves as a source of electrons; 3·5 mm. away from the tungsten wire is a platinum gauze. The electrons emitted are drawn toward the gauze by an accelerating potential difference, V_a; some pass through the gauze, but then encounter a retarding potential difference, V_r, which is sufficiently greater than V_a to prevent any electrons reaching the electrode. This electrode is connected to a quadrant electrometer, and may gain a positive charge either from positive ions produced by ionisation of the gas or as a result of electrons emitted photoelectrically by ultra-violet radiation set up by impacts of the electrons. The electrode is 7 mm. distant from the gauze. The electrode consists of a ring of copper closed at one side by a thin platinum foil, and at the other by a platinum gauze. It is suspended on a platinum wire, and so arranged that either the gauze or foil may be presented to the radiation. Positive ions are received by the electrode equally well whichever side is presented to the radiation, but the two sides are differently affected by ultra-violet radiation, for when the gauze is presented, a large part of the radiation enters the electrode and does not result in a loss of electrons. Thus the ratio E_f/E_g of the electrometer deflexion with the foil or gauze exposed gives the proportion of the total effect which is due to both of the individual effects. Using this apparatus with helium it is found that resonance radiation sets in at 20·2 volts and ionisation at 25·5 volts. Ionisation is observed between 20·2 and 25·5 volts in proportions increasing with the gas pressure and with the bombarding current density. Evidence is presented to show that this ionisation is a secondary effect, due to impacts against electrons which contain absorbed radiant energy of the resonance radiation from neighbouring atoms. This method of ionisation appears to be very important at high gas pressures. The present results are a complete confirmation of those of Horton and Davies (A., 1919, ii, 210). J. F. S.

Distribution of the Emission Intervals of the α-Particles of Polonium. (MME) MARIE CURIE (*J. Phys. Radium*, 1920, [vi], 1, 12—24).—The intervals between the emission of α-particles by polonium have been studied in the case of 10,000 emissions from several preparations of the polonium used in connexion with the work on its spectrum and its change into lead. The emissions were recorded by an electrometer provided with a photographic arrangement for registering the deflexions caused by the individual α-particles. The results had to be corrected for the slow decay of the activity of the polonium and for the failure of the electrometer to distinguish emissions separated by less than a certain minimum interval (doublets). The law derived from the theory of probability, that if θ is the mean interval, the fraction of the total intervals of duration greater than τ is $\epsilon^{-\theta/\tau}$, was completely

verified by the experiments. Curves in which the logarithm of the number of emissions, of interval greater than a given interval, are plotted against this interval, are straight lines, except for the smallest intervals (due to doublets, which can so be evaluated) and the longest, where the number is too few for the result to be accurate. By suitably combining all the results in one curve, a verification to an extreme degree of accuracy was obtained. The radioactive constant, λ, for polonium was redetermined, and found to be 0·00496(day)$^{-1}$, corresponding with a period of average life of 202 days, and of half change, 140 days, in agreement with the accepted value. F. S.

Radioactive Analysis of the Thermal Springs of Bagnères-de-Luchon, Springs very Rich in Radium Emanation. ADOLPHE LEPAPE (*Compt. rend.*, 1920, **171**, 731—733).—The waters from the various springs of Bagnères-de-Luchon were found to contain from 0·4 to 41·5 millimicrocuries of radium emanation per litre, and they thus form some of the most radioactive springs in the world. W. G.

The Variations of the Radioactivity of the Springs of Bagnoles-de-l'Orne and their Relation to the Rain. P. LOISEL (*Compt. rend.*, 1920, **171**, 858—860. Compare A., 1919, ii, 489).—The radium emanation content of the water of the springs at Bagnoles-de-l'Orne shows considerable variation, and this is correlated with the rainfall. The amount of radium emanation present rises and falls with increase or diminution in the rainfall, but the interval between maximum rainfall and maximum emanation content varies with the particular spring, and presumably depends on the nature of the strata through which the rain must percolate before reaching the spring. W. G.

The Electrical Conductivity of Potassium, Sodium, and Barium Chlorides in Mixtures of Pyridine and Water. JNANENDRA CHANDRA GHOSH (T., 1920, **117**, 1390—1396).

Hydrogen Overvoltage. EDGAR NEWBERY (*J. Amer. Chem. Soc.*, 1920, **42**, 2007—2011. Compare MacInnes and Adler, A., 1919, ii, 131; MacInnes and Contieri, this vol., ii, 77).—A criticism of the above-mentioned papers. It is stated that the definition of overvoltage given is incorrect, and that the measurements recorded are not overvoltage measurements, but the excess potential necessary to overcome the transfer resistance, which in the experiments may have had values from 1000—100,000 ohms. The statements made about the dimensions of the overvoltage of platinum are incorrect. The hypothesis put forward is quite unable to account for the dependence of overvoltage on valency and many other phenomena, which are readily explained by the hydride or higher oxide hypothesis. The effect of pressure on overvoltage observed is due to changes in transfer resistance (see T., 1914, **105**, 2428). J. F. S.

Stability of the Cobaltammines. ARTHUR B. LAMB and ALFRED T. LARSON (*J. Amer. Chem. Soc.*, 1920, **42**, 2024—2046).—The oxidation potentials of six representative cobaltic ammines have been measured in 3·265*M*-ammonium hydroxide solution. From these potentials, the concentration of the simple cobaltic ion in these solutions has been calculated, and the relative stability of the ammines ascertained. The stability is very great compared with that of other metallic ammines. The six ammines, arranged in order of stability, are: aquo-pentammine cobalt chloride, diaquo-tetramminecobalt chloride, 1:2-dinitro-tetramminecobalt chloride, nitro-pentamminecobalt chloride, hexamminecobalt chloride, and 1:6-dinitrotetramminecobalt chloride. The stability constants of a number of metallic ammines are calculated, and the following values obtained: $Ag(NH_3)_2$, $6·8 \times 10^{-8}$; $Cu(NH_3)_2$, $1·5 \times 10^{-9}$; $Cd(NH_3)_4$, $1·0 \times 10^{-7}$; $Zn(NH_3)_2$, $2·6 \times 10^{-10}$; and $Co(NH_3)_6$, $1·25 \times 10^{-5}$. A series of other measurements have been made to obtain the data necessary in the above-named calculations; these include: (i) The measurement of the potential of the cobalt cobaltous electrode in cobalt chloride solutions at 25°, from which the normal potential $Co/Co^{\cdot\cdot}$ at 25° is found to be −0·237 volt. (ii) The measurement of the potential of the cobalt cobaltous electrode in solutions of cobalt chloride in 6*M*-ammonium hydroxide, from which the formula of the cobaltous ammine ion is shown to be $Co^{++}(NH_3)_6$, and the equilibrium constant for its dissociation into ammonia and the simple cobaltous ion is shown to be $1·25 \times 10^{-5}$. (iii) The normal $Co^{\cdot\cdot}/Co^{\cdot\cdot\cdot}$ potential at 0° and 16° has been measured, and that at 25° extrapolated. The values obtained are: 0°, 1·775 volts; 16°, 1·779 volts; 25°, 1·817 volts. The temperature-coefficient of this value is +0·00169 volt. (iv) The potential of the hydrogen electrode in 2*M*-sulphuric acid has been measured against the normal calomel electrode at 0° and 16°, when the values obtained for the combination

$$Hg | Hg_2Cl_2 | MKCl | sat. NH_4NO_3 | H_2SO_4 2M | H_2$$

were: 0°, +0·2878 volt, and 16°, 0·2816 volt. On the assumption that the normal hydrogen electrode has a zero temperature-coefficient, these give for the single potential $H_2 | 2MH_2SO_4 \|$ the values 0°, +0·0012 volt, and 16°, +0·0047 volt, when Auerbach's values for the calomel electrode are employed (A., 1912, ii, 123).

J. F. S.

Electrode Processes. Influence of Rise of Temperature and Depolarisers on the Form in which Nickel Separates. HANS STÄGER (*Helv. Chim. Acta*, 1920, **3**, 584—613).—In order to throw further light on the connexion between polarisation and the form of metals deposited electrolytically, developed by Kohlschütter and Vuilleumier (A., 1919, ii, 9), the author has investigated (1) the formation or alteration of deposits of nickel under conditions effecting depression of the polarisation, and (2) the behaviour of these deposits when the development of the film of hydrogen, regarded as the true cause of the highly disperse metallic deposits, is suppressed by means of cathodic depolarisers.

As regards the course of the contraction of nickel deposits from different electrolytes, two types exist, the contraction in the one case gradually diminishing, whilst in the other it increases somewhat. The temperature at which the layer is formed influences the structure, and consequently the mechanical behaviour, of the deposit; since the development of a film of gas at the electrode must be rendered difficult by rise of temperature, the diminished dispersivity, and the resultant diminished capacity to sinter, which are observed may well be due to decrease in the deposit of hydrogen.

The experiments carried out on solutions containing depolarisers, such as hydrogen peroxide, nitrobenzene, potassium chlorate, and sodium cinnamate, show that the contraction of the nickel deposits is markedly diminished and their structure altered under these conditions, as should be the case if the discharged hydrogen is the ultimate cause of the effect. The results obtained when an alternating current is superposed to the direct current used for the electrolysis are also described. T. H. P.

Nature of the Spontaneous Alterations in Structure of Nickel Deposits. V. KOHLSCHÜTTER (*Helv. Chim. Acta*, 1920, **3**, 614—620).—The results obtained by Stäger (preceding abstract) and others are discussed. T. H. P.

An Electrolytic Current Intensification Effect, a New Electrolytic Displacement Effect and the Connexion between Electrolysis and the Emission of Electrons in a Vacuum. D. REICHENSTEIN (*Zeitsch. physikal. Chem.*, 1920, **95**, 457—507).—A theoretical paper in which it is shown that the conversion of an alternating current into a direct current by means of an electrolytic cell containing a passive metal cannot in any way be determined by the static characteristics in both directions, but only the dynamic characteristics are capable of giving information on such a transformation. The Schlömilch cell connected with a source of current is not only a detector, but, at the same time, a current intensifier. A scheme is described, useful in wireless telegraphy, whereby a strong intensification of current may be brought about electrolytically. This current intensification is an effect of the displacement principle. The action of the Schlömilch cell is explained on the basis of the new intensification effect. The potential difference electrode | vacuum may be calculated in exactly the same way as that existing between zinc and an aqueous solution of zinc ions. The electron emission in a vacuum can be expressed in the same way as electrolysis in chemical kinetic terms, whereby the divergences from Richardson's relationship and from Langmuir's spacial charge equation may be explained. These two relationships can only be regarded as limiting expressions.

J. F. S.

Hydration of Electrolytic Ions. RICHARD LORENZ (*Zeitsch. Elektrochem.*, 1920, **26**, 424—431).—A theoretical paper in which,

making use of the author's work on space filling and the mobility of ions (*this vol.*, ii, 481), it is shown that, by means of a modification of Stokes' law (Born. A., 1919, ii, 214; *Zeitsch. Physik*, 1920, **1**, 220), the amount of hydration of electrolytic ions may be calculated. The space-filling number increases in proportion to the cube of the radius of the molecule, and, having determined the radius of the ion from the mobility by means of the modified Stokes law, the amount of hydration may be calculated. In the present paper, the hydration of ions is looked on as a sheath of water molecules round the ion, which is not necessarily made up of a simple number of molecules. The order in which the mobilities of the ions of the alkali metals occur is in quite the wrong direction for the atomic weights, but in view of the present arguments, the order of the mobilities is shown to be correct. Lithium possesses the smallest electrodynamic radius, and therefore moves most slowly, whilst cæsium possesses the largest electrodynamic radius and moves fastest. J. F. S.

Disappearance of Gas in the Electric Discharge. THE RESEARCH STAFF OF THE GENERAL ELECTRIC CO., LTD., LONDON (*Phil. Mag.*, 1920, [vi], **40**, 585—611).—The present paper gives an account of an attempt to ascertain the cause of the disappearance of gas under an electric discharge at low pressure. Previous knowledge on the subject is briefly summarised. The parts played by absorption on the walls by chemical combination are unknown; it is also unknown what electrical conditions most favour the disappearance. Preliminary observations showed that the disappearance of gas was closely connected with the appearance of the glow in the vessel. In any given state of the discharge vessel, the glow appears sharply at a definite potential difference between the electrodes; this is termed the glow potential. The relationships existing between the glow potential and the thermionic emission, the pressure of the gas, the nature of the gas, and the form of the electrodes, respectively, have been examined. Small amounts of impurity change the glow potential very markedly, particularly in hydrogen. The general connexion between the appearance of the glow and the increase of ionisation is considered. The great importance of the glow potential for interpreting the rate of disappearance of gas is indicated. A number of experiments on the disappearance of carbon monoxide in the glow discharge are described. The results are discussed and explained by supposing that the glow causes a chemical change in the gas, which is reversible. The recognition of the reversibility appears necessary to explain the phenomena. J. F. S.

The Thermal Variation of the Coefficient of Magnetisation of Anhydrous Sulphates and the Theory of Magneton. PH. THÉODORIDÈS (*Compt. rend.*, 1920, **171**, 715—717).—If X is the specific coefficient of magnetisation in the case of each of the three anhydrous sulphates studied, namely, manganous, cobaltous, and ferric sulphates, the curve showing $1/X$ as a func-

tion of the temperature consists of two parallel straight lines joined by a short, curved portion. In the case of two of the sulphates, this discontinuity is very close to the point at which the monohydrate loses its water, and it may therefore be due to a trace of impurity. In all these sulphates the molecular field is negative, and their virtual Curie point is below absolute zero. The results obtained conform with the theory of magneton. W. G.

A Thermo-regulator. J. FITCH KING (*J. Amer. Chem. Soc.*, 1920, **42**, 2058).—A device is described to prevent the contamination of the mercury surface in thermo-regulators which operate an electrical control of the heating arrangements. The contamination of the surface is due to oxidation when the small arc is produced at each break of the contact between the mercury and the wire contact. This can be avoided by replacing the air in the regulator by nitrogen. To do this, a small bulb is blown in the capillary tube at a short distance above the mercury surface, and in this bulb a globule of mercury is placed, so that a small volume of the tube is entirely cut off from the atmosphere. The wire contact passes through the globule, and can then make its contact in the usual way. The mercury globule rises and falls with the mercury surface below, but it never slips down and joins the lower mercury surface. The air space between the two mercury surfaces may be filled with nitrogen, but there is no need for this, as the small amount of oxygen is speedily used up, and then the surrounding gas is inert. J. F. S.

Determination of the Thermal Conductivity of Water. MAX JAKOB (*Ann. Physik*, 1920, [iv], **63**, 537—570).—A new method for the determination of the thermal conductivity of liquids is described. The thermal conductivity of water has been determined from 7·4° to 72·6°. A table of results is given, which may be represented by the formula $\lambda = 0{\cdot}4769(1 + 0{\cdot}002984t)$, in which the units are $Cal. m.^{-1} hour^{-1} degree^{-1}$. In *C.G.S.* units ($cal. cm.^{-1} sec.^{-1} degree^{-1}$), the formula is

$$\lambda = 0{\cdot}001325(1 + 0{\cdot}002984t).$$

The results are correct to 1%. J. R. P.

Radiation in Explosions of Hydrogen and Air. W. T. DAVID (*Proc. Roy. Soc.*, 1920, [*A*], **63**, 183—198).—Mixtures of hydrogen and air were exploded in a closed vessel with black walls. The proportion of heat of combustion lost by radiation during explosion and cooling decreases greatly with the mixture strength. The total radiation emitted is a linear function of the maximum temperature developed. The proportion of heat lost by radiation up to the moment of maximum temperature varied between 0·5% (strongest mixture) and 1·4% (weakest mixture). The maximum rate of emission occurs approximately at the point of maximum temperature. Weak mixtures radiate more strongly in the initial stages of cooling than stronger mixtures when they have cooled to the same mean temperatures. The rate

of emission in the strongest mixture is approximately proportional *to the fourth power of the absolute temperature.* This does not hold in the initial stages of cooling of weak mixtures, but holds satisfactorily in the later stages. The 2·8 μ emission band of steam ceases to be emitted when the temperature has fallen to about 1000° abs. The radiation contains wave-lengths greater and less than this. In experiments with silvered vessels, it was found that the intrinsic radiance increases with the size of the vessel, and the gases after explosion are very transparent throughout, cooling to radiation of the same kind as they emit.

The results are taken to indicate that the vibratory degrees of freedom of the steam molecules corresponding with radiation of 2·8 μ share the heat energy of the molecules only above 1000° abs., and this may account for the rapid increase of specific heat in this region. J. R. P.

The Specific Heat of Saturated Vapours at Low Temperatures. G. BRUHAT (*Compt. rend.*, 1920, **171**, 712).—A reply to Ariès (this vol., ii, 585). W. G.

Aggregation at the Melting Point. WILLIAM R. FIELDING (*Chem. News*, 1920, **120**, 241—242, 255—256, 302—303; **121**, 87—88, 150—153).—At the melting point, the molecules of each element are aggregated in a definite manner to form "melticules." The "melticular weights" of elements increase with the melting point. If the melting points are plotted against the melticular weights, all the elements lie on a single parabolic curve; if the melting points are close together, the curve is nearly a straight line. The rate of aggregation, R, is found by dividing the melticular weight by the molecular weight. If the quotient sp.ht./R is plotted against the melting point, the elements considered lie on a parabolic curve, but if m.pt. × sp.ht. is plotted against R, the curve is nearly a straight line.

The specific heat is calculated by the formula

$$\text{m.pt.} \times \text{sp.ht.}/R = 4{\cdot}15.$$

A table of melticular weights and values of R is given. All elements with abnormally low specific heats are polymerised. In each group of elements (with occasional exceptions), and very often in the same series, the specific heat falls with increase of atomic weight. The considerations are applied to compounds. J. R. P.

Clausius' Vaporisation Formula and a Comparison of the Vapour-pressure Curves of Two Substances. FR. A. HENGLEIN (*Zeitsch. Elektrochem.*, 1920, **26**, 431—436).—The Ramsay-Young and the Dühring rules have been deduced from the Clausius vaporisation formula, and thereby the physical significance of the constants occurring in these formulæ has been demonstrated. Dühring's rule is a special case of the general formula $kT_1\theta_1/T_2\theta_2 = (T_1-\theta_1)/(T_2-\theta_2)$, which holds even at high temperatures, and in which T_1 and θ_1 are the boiling points of a substance

at two different pressures, and T_2 and θ_2 the boiling points of another substance at the same two pressures. The constant k is approximately equal to the relationship between the molecular heat of vaporisation of the two substances. A formula is developed from the Clausius vaporisation formula which has the form $\log T_1 = a \log T_2 + b$. This formula holds exactly up to the critical point. In this formula, T_1 and T_2 are the temperatures at which both substances possess the same vapour pressure; a and b are constants. The constant a has a value between 0·8 and 1·5, and should it be exactly unity, the formula becomes the simplified Ramsay-Young formula. This equation is tested on a large number of substances in comparison with water. The agreement between the known experimental values and the calculated values is very good, so that it is practically possible to determine the vapour-pressure curve of a substance from that of water. The vapour-pressure regularities recently found by Herz (A., 1916, ii, 311) are explained. J. F. S.

Finiteness of the Expression $\int_0^T C/T . dT$ in Wegscheider's Vapour-pressure Formula. F. MAY (*Zeitsch. physikal. Chem.*, 1920, **95**, 434).—A theoretical paper in which it is shown that the integral mentioned in the title becomes at the lower limit an infinite function, and, further, the integral has no definite value, since $\int_0^T a'/T . dT = a' \lim_{\epsilon=0} \int_{0+\epsilon}^T = +\infty$, a condition which Wegscheider (this vol., ii, 598) has not taken into account in his vapour-pressure formula. J. F. S.

Finiteness of the Expression $\int_0^T C/T . dT$. RUDOLF WEGSCHEIDER (*Zeitsch. physikal. Chem.*, 1920, **95**, 435—437. Compare preceding abstract).—An answer to May's criticism of the author's vapour-pressure formula, in which the use of the integral in question is justified. J. F. S.

Normal Vapour Pressures. C. VON RECHENBERG (*J. pr. Chem.*, 1920, [ii], **101**, 112—122).—The present difficulty in making comparisons between the boiling points of substances determined under differing, diminished pressures leads the author to propose the adoption of a second standard pressure, which could be achieved by using a fraction of the physical atmosphere (760 mm.) or of the technical atmosphere (737 mm.), or a multiple of the absolute unit of pressure of the thermodynamic scale of the *C.G.S.* system. The latter course appears preferable, and a standard pressure equal to 15 mm. of mercury is suggested.

In the determination of boiling point under considerably reduced pressure, errors in the reading of the manometer are shown to be far more serious than those caused by incorrect reading of the thermometer.

On the basis of the Crafts-Young formula, the boiling points

of substances can be calculated to 15 mm., in accordance with the expression $C = x(15 - p)(273 + t)$, in which t is the approximately estimated boiling point under 15 mm. pressure, x is a coefficient depending on the nature of the substance, and C is the correction to be applied. In utilising the formula for the calculation of boiling point at atmospheric pressure, it is found adequate to divide substances into two classes, for one of which the mean value of x is 0·00010, and for the other 0·00012; for pressure below 25 mm., however, a further subdivision is necessary, and the following values of x are calculated from the recorded boiling points at 14—15 and 15—16 mm.; 0·004187 for hydrocarbons, ethers, oxides, thiocarbimides, mercaptans, sulphides, nitriles, and acid chlorides; 0·004009 for ketones; 0·003946 for esters, amines, and aldehydes; 0·003720 for phenols; 0·003574 for acids; 0·003458 for alcohols; 0·00301 for hydrazones; 0·002835 for quinones. The entrance of chlorine, bromine, or iodine atoms, or of the nitro-group, into a compound has less effect than isomerism on the coefficients. The calculations, both for 760 mm. and 15 mm., are only valid in the total absence of dissociation or other transformation. The calculation for 15 mm. is not designed for the correction of a boiling point determined at any reduced pressure to this particular value; if it is to be employed, the determination must be effected in such a manner that the reading of the manometer, which must be affixed to the boiling tube, only differs slightly from 15 mm. H. W.

Some Applications of the Method of Distillation in Steam. JOSEPH REILLY and WILFRED J. HICKINBOTTOM (*Sci. Proc. Roy. Dubl. Soc.*, 1920, **16**, 131—142).—The suitability of the distillation method for determining molecular structure is discussed, but a consideration of the distillation constants of a number of compounds shows that, although the molecular structure may be inferred in certain cases, this method cannot be applied generally without the support of further evidence.

The distillation of solutions containing a volatile solute can be applied to detect changes in the state of molecular aggregation.

By reason of the fact that butter-fat contains appreciable amounts of butyric acid, whilst this acid does not occur in appreciable amounts in other fats of the type examined, butter-fat may be differentiated from these fats by the method of analysis of solutions by distillation. [See also *J. Soc. Chem. Ind.*, 1920, 804A.] W. G.

Calorimetric Procedure for Determining the Heats of Slow Reactions. II. Calorimetry of a Slow Reaction: Heat of Inversion of Sucrose by Acids. FREDERICK BARRY (*J. Amer. Chem. Soc.*, 1920, **42**, 1911—1945. Compare this vol., ii, 533).—A method is described whereby the heat of inversion of sucrose by hydrochloric acid is measured with a precision largely determined by the characteristic errors of precise mercury thermometry. This reaction is exothermal, and involves a partial con-

current and endothermal heat of mixture, which, under favourable conditions, continues for nine hours. The adiabatic method, which alone is applicable in such determinations, is thus shown to be generally adequate for the precise calorimetric measurement, not *only of swift reactions, but of any reaction which at ordinary* temperatures requires less than a day for its completion. A way is thus indicated whereby chemical, kinetic, and total energy data may, in general, be directly correlated. The process itself is illustrative of such correlation. Incidentally, the procedure suggests a general and uniform method for the precise determination of adiabatic velocity-coefficients, and thus of the temperature-coefficients of velocity constants, by energy measurements alone. A number of modifications of the usual calorimetric practice are described. These are necessary for the measurement of the heats of slow reactions, but they are also generally applicable. Notice is taken of the probable source of error in mercury thermometry, due to the effect of radiation on encased thermometer threads. The following experimental data have been obtained: heat of inversion of sucrose by hydrochloric acid at 20°, 10·4±0·06 gram cals. per gram; heat of solution of sucrose in water at 20°, 3·43±0·02 gram cals. per gram for solutions up to about 4% sucrose concentration; heat of solution of sucrose in 1·64*N*-hydrochloric acid, 4·23±0·05 gram cals. per gram for solutions containing up to 4% sucrose; heat of solution of anhydrous *α*-glucose in water at 20° and in 1·64*N*-hydrochloric acid at the same temperature, 13·9±0·1 gram cals. per gram for solutions containing up to 4% glucose. J. F. S.

The Principle of the Constant Sum of the Energy of Formation and its Partition between the Atomic Linkings in Aromatic Substances. A. L. von Steiger (*Ber.*, 1920, **53**, [*B*], 1766—1772).—In a previous paper (this vol., ii, 355), the energy of the C–C and C–H linkings in aromatic hydrocarbons was calculated, on the supposition that, in six-ring or condensed six-ring systems, the C–C and C–H linkings, respectively, are all equivalent. It is certain, however, that in such compounds all C–H linkings are not equivalent (in naphthalene, for example, the *α*- and *β*-hydrogen atoms have different reactivities), but since the heat of combustion can be accurately calculated from constant x and y values for all C–H and C–C linkings, it follows that there must be some compensating effect at work. A principle of partition of the energy of the atomic linkings is worked out on the assumption that all the energy values may be different, and that the heat of decomposition of a $>$CH group is $k_1=y+x$, and that of a carbon atom united to three others, $k_2=3/2y$, where x and y have the same significance as above. In other words, the sum of the energies of the linkings of each carbon atom is regarded as constant, instead of the energy of each C–C and C–H linking. In applying these assumptions to the consideration of hypothetical cases, it is assumed that when the energy of one linking of a carbon atom is increased, that of each of the two others is correspondingly

decreased. (*Each aromatic carbon atom is regarded as tervalent, loc. cit.*) It is shown that a change in the energy value of one such linking affects all the carbon linkings in the system, the effect diminishing as the distance from the disturbance becomes greater.

The energy value of the C–C linking in aromatic compounds is greater than in aliphatic compounds, and in the case of an aromatic–aliphatic linking, the value must lie between these two. For example, in toluene, the energy value of the side-chain C–C linking is higher than in an aliphatic compound, and the value for each C–H linking in the $-CH_3$ group is correspondingly lowered, according to the above principle, with the result that the *side-chain hydrogen atoms are more reactive in toluene than in ethane.*

E. H. R.

The Relation between the Physical Properties of some Organic Liquids. W. HERZ (*Zeitsch. anorg. Chem.*, 1920, **112**, 278—282. Compare this vol., ii, 414).—In a former paper (this vol., ii, 285) it was shown that the quotient of the critical temperature and the critical pressure, T_k/p_k, divided by the sum of the valencies of the atoms in the molecule, z, is equal to a constant, 0·44, for a large number of non-associated compounds. Combining this with the expression $T_k = \frac{1}{2}(1/k_{20} + 293)$, where k_{20} is the *coefficient of expansion at 20°, the critical pressure can be calculated* from a knowledge of k_{20} and z. This has been done for a number of liquids of the aliphatic and aromatic series, with fair agreement between observed and calculated values of p_k. A relation is also deduced between molecular weight, critical density, and number of valencies, which is expressed by $d_k = M/9{\cdot}24z$. This relation is checked against a large number of liquids of known critical density. The critical molecular volume assumes the simple form $MV_c = 9{\cdot}24z$. From the relation $L = 0{\cdot}666p_k/d_k$, where L is the heat of evaporation at the boiling point, combined with the above relationships, it follows that L can be calculated from a knowledge of k_{20}, d_k, and z, or from k_{20} and the molecular weight by the equation $L = 0{\cdot}6993(1/k_{20} + 293)/M$. E. H. R.

Comparative Method for Determining Vapour Densities. II. PHILIP BLACKMAN (*J. Physical Chem.*, 1920, **24**, 267—276).—A weighed amount of the substance is introduced into one limb of a U-tube over mercury. Air is present in both limbs. The apparatus is then heated in a bath until the substance is completely vaporised. Formulæ for calculation of the vapour density are given. J. R. P.

A Relation between the Volume and the Viscosity of some Organic Ions. HOMER W. SMITH (*J. Physical Chem.*, 1920, **24**, 539—561).—The velocity of an organic ion is independent of the mass of the ion and of its configuration. It depends essentially on two factors, namely, the specific nature of the nucleus or polar group to which the ion owes its chemical properties, and the total volume of the ion. In any series of ions

having a common ionic nucleus, and no other (namely, $-COO'$, $-NH_3'$, $-NH'$, etc.), and apart from certain well-defined disturbing influences, the velocity is an inverse exponential function of the volume. J. R. P.

Fluidities and Specific Volumes of Mixtures of Ethyl Benzoate and Benzene. EUGENE C. BINGHAM and LANDON A. SARVER (*J. Amer. Chem. Soc.*, 1920, **42**, 2011—2022).—The viscosity and density of mixtures of benzene and ethyl benzoate of a series of compositions have been measured at temperatures from 5° to 75°. From the experimental data, specific volume–temperature, fluidity–temperature, and fluidity–specific volume curves have been constructed. It has been stated that when inert liquids are mixed, the fluidity is a linear function of the volume composition. Benzene and ethyl benzoate neither undergo contraction nor is there any development of heat on mixing; they are therefore to be regarded as inert towards one another. At 25°, the fluidity–volume concentration curve is not linear, and the cube roots of the viscosities are a linear function of the molecular concentration. This indicates that benzene and ethyl benzoate must show quite perceptible concentration on mixing, which is proof of the aggregation demanded by the fluidity–volume concentration curve. Furthermore, the cube-root equation applies at only the one temperature used in the earlier work, but it does not apply at either higher or lower temperatures. This example is therefore not only not evidence against the fundamental hypothesis that fluidities are additive, but it furnishes strong evidence in its favour. J. F. S.

The Sorption of Copper Sulphide. K. SCHERINGA (*Pharm. Weekblad*, 1920, **57**, 1294—1295. Compare A., 1918, ii, 409; 1919, ii, 367).—A curve given previously by the author for the carrying down of sodium chloride from solution by precipitated copper sulphide is found to hold only for very narrow limits; at different concentrations, very different quantities are carried down. The formation of a precipitate is probably preceded by the separation of structureless particles, surface tension being stronger than the directive force of crystal formation; these particles are able to adsorb other substances, a property which disappears as crystal formation sets in. S. I. L.

Sorption of Cellulose (Filter-paper) and Starch. Imbibition. K. SCHERINGA (*Pharm. Weekblad*, 1920, **57**, 1289—1294).—The adsorptive power of filter paper is largely due to the distensible capillaries, which give it the character of a rather coarse, disperse medium. Since cellulose acts in water as a negative colloid, solutions of negative colloids, such as the metal sulphide sols, are stable towards it, whereas positive colloids, such as the metal oxide sols, are flocculated and suffer adsorption. The adsorption of neutral salts is slight, being relatively greater with more dilute solutions. The same is true for alkalis and alkaloids, but here the

adsorption is greater, and is completely inhibited by traces of acid. Since filter paper takes up ammonia and carbon dioxide from the air, all experiments were carried out with sheaves of paper dried at 120°.

In the case of starch, the behaviour is less simple, depending on the degree of hydration, the temperature employed, etc., but here also adsorption was relatively greater with more dilute solutions and largely inhibited by traces of acid. S. I. L.

Deduction of the Dissociation Equilibrium from the Theory of Quanta and a Calculation of the Chemical Constants. P. Ehrenfest and V. Trkal (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 162—183).—A mathematical paper in which the conditions of equilibrium of a dissociating gas are deduced by statistical methods from the quantum theory. The relation between probability and entropy is discussed, and the ordinary calculations are extended by taking account of the grouping and motion of the atoms in the molecules. A vapour-pressure formula for very low temperatures is deduced.

On comparing the dissociation equation deduced with the corresponding thermodynamic equations, values are obtained for the chemical constants in the latter. J. R. P.

Explanation of an Apparent Anomaly Outstanding in the Results of the Measurement of Dissociation Pressures. Alan W. C. Menzies (*J. Amer. Chem. Soc.*, 1920, **42**, 1951—1956).—The experimental dissociation pressures of Tammann (A., 1888, 403), Schottky (A., 1908, ii, 1016), and Partington (T., 1911, **99**, 466) have been outlined so as to elucidate an anomaly which is outstanding at the present time, namely, that the dissociation pressures of salt hydrates appear higher when measured by the gas current saturation method than when measured by the tensimetric method, and that tensimetric measurements yield readings which are greater at the beginning of the experiment than at the end. The explanations of this discrepancy put forward by Tammann (*loc. cit.*), Nernst (*Zeitsch. physikal. Chem.*, 1908, **64**, 425), Campbell (A., 1915, ii, 516), Partington (*loc. cit.*), and Brereton Baker (*Ann. Reports*, 1912, **8**, 34) are considered. A number of criticisms and suggestions in connexion with both methods are put forward. The dissociation pressure has been redetermined for copper sulphate pentahydrate by both methods, and the results of previous workers confirmed. It is shown that the results of the gas-current method are, as was to be expected to be, a little higher than those of the tensimetric method, and that the discrepancy observed is well within the experimental error of such measurements, consequently there ceases to be an anomaly. It is shown that the tensimetric results of Froweiu (A., 1888, 337), often regarded as standards, should be accepted with caution.

J. F. S.

Theoretical Investigations of the Condition of Dissociation. II. A. The Influence of Bivalent Ions. B. The nfluence of Colloidal Condition. L. MICHAELIS (*Biochem. Zeitsch.*, 1920, **106**, 83—91).—A theoretical paper. S. S. Z.

Spontaneous Velocity of Diffusion of Molten Lead. . GRÓH and G. VON HEVESY (*Ann. Physik*, 1920, [iv], **63**, 85—92). -The spontaneous diffusion of molten lead has been determined y placing a layer of molten lead above a layer of a radioactive ead isotope (thorium-*B*) in a narrow, hard glass tube, and placing he tube in an upright position in a furnace of constant temperaure for periods varying up to two days. After cooling, the lead as cut into sections, and the α-ray activity measured in each iece. From the measurements, the quantity which had diffused o various heights was calculated. The results of seventeen experiments show, as a mean value, that 2·2 grams diffuse through an rea of 1 sq. cm. per day at 343°. This value has been reduced o ordinary temperature and the viscosity of water, and the value ·1 grams cm.^{2}/per day obtained. This value is approximately hree times as large as the velocity of diffusion of the lead ion in ater, from which is deduced that the radius of the lead ion is at east three times as large as that of the lead molecule in molten ead, and in consequence the lead ion is regarded as being heavily ydrated. J. F. S.

Osmotic Pressure Regarded as a Capillary Phenomenon. I. HULSHOF (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 84—192).—A mathematical discussion of osmotic pressure on the asis of molecular attraction. J. R. P.

Planck's Theory of Dilute Solutions. P. BOEDKE (*Physikal. Zeitsch.*, 1920, **21**, 551—552).—An extension of a former paper his vol., ii, 229). Retention of terms of the second order in espect of concentrations in the expression for the potential is not ufficient to include known cases of equilibria. J. R. P.

The Irregular Series of Flocculation. H. R. KRUYT and MME) H. G. VAN ARKEL-ADRIANI (*Rec. trav. chim.*, 1920, **39**,)9—614).—From a study of the flocculation of neutral and kaline gold sols by thorium nitrate and by colloidal thorium ydroxide, the authors conclude that, as a general rule, the regular series are produced by the strong electro-capillary action the ions, which discharge. It is only in the case of the intenonal formation of an hydroxide sol, in alkaline medium, that the henomenon of reciprocal flocculation occurs. W. G.

The Relation between the Limit Value and the Concentration of Gold Sols. H. R. KRUYT and A. E. VAN ARKEL Rec. trav. chim., 1920, **39**, 615—617. Compare preceding bstract).—It has previously been shown for a sol of arsenious

sulphide that with the potassium ion the limit value increases with dilution of the sol, whilst with the barium ion it remains almost constant, and diminishes considerably with the aluminium ion. It is now shown that in the case of a gold sol the limit value increases either with a potassium, barium, or aluminium ion, and only diminishes slightly with the quadrivalent thorium ion.

W. G.

The Critical Potential. H. R. KRUYT (*Rec. trav. chim.*, 1920, **39**, 618—622).—A theoretical discussion of previous work (preceding abstracts), in which it is shown that for a given disperse substance the critical potential is only a constant within certain limits. It is necessary to take into account also the probability of adhesion. W. G.

Thermo-kinetic Explanation for the Reciprocal Attraction of Colloidal Particles. (A Possibility of Explaining Gravitation.) ROBERT FRICKE (*Zeitsch. physikal. Chem.*, 1920, **95**, 441—456).—A theoretical paper in which the reciprocal attraction between colloidal particles in solution is shown to be due, in part, to kinetic actions, and not entirely to molecular attraction. The same conclusion is drawn for gas disperse systems, and a thermo-kinetic "shadow" hypothesis developed. This thermo-kinetic "shadow" hypothesis is further developed to a general energetic shadow hypothesis, which, on certain assumptions, is applied to other physical problems, particularly gravitation.

J. F. S.

The Formation and Stability of Colloidal Solutions. P. P. VON WEIMARN (*Ann. école mines de l'Oural*, 1919, **1**, 14—16). —Theories of the stability of colloidal solutions which are based entirely on the influence of ions, such as that of Malfitano (A., 1911, ii, 102), cannot be of general application, for, just as concentrated true solutions of a substance can be obtained in a solvent in which it is practically non-ionised, so can stable colloidal solutions of any substance be made in non-ionising solvents. Colloidal solutions of a substance in a dispersion medium in which it does not form a true solution cannot be prepared in more than very limited concentration unless a dispergator (peptising agent) be present. CHEMICAL ABSTRACTS.

The Fundamental Principles of Synthesis of Dispersoids in the Light of my Researches from 1906 to 1916. P. P. VON WEIMARN (*Ann. école mines de l'Oural*, 1919, **1**, 1—5). —(*A*) General principles. (1) Any substance may be obtained in any degree of dispersion. (2) During solution of any substance in any solvent, the substance passes through the dispersoid state. Near a transition point the substance is in the dispersoid state. (*B*) Conditions for the dispersoid state irreversible with temperature. (I) Dispersoid solutions of low concentration result from reactions

producing the substance in a medium in which it is only slightly soluble, provided the reacting substances are very dilute. (II) Dispersoid solutions of higher concentration. (1) These coagulate at once in media which are practically completely indifferent to the disperse phase. (2) For the preparation of dispersoid solutions of higher concentration, conditions of dispergation (peptisation) (A., 1909, ii, 306; "Grundzüge der Dispersoidchemie," 1911, 76) and of dispersoid parasitism must obtain. (3) Homochemical compounds (barium sulphate forms homochemical compounds with all barium salts and all sulphates) exist for every substance and make it possible to realise conditions of dispergation and dispersoid parasitism. (III) Dispersoid precipitates. (1) These are obtained for any substance by carrying out the reaction forming it in a medium in which it is very slightly soluble. (2) A high degree of dispersion exists the longer the lower the solubility in the medium and the more indifferent to it. (3) The homo- and hetero-chemical cohesive forces exerted on the disperse phase by the dispersion medium and by substances in solution in it retard the union of the particles of dispersed phase, and hence the velocity of crystallisation. (C) Principles governing the dispersoid state reversible with temperature. (1) Any substance can be obtained by slow cooling of its solution as a highly dispersed gel or glass, which can be dissolved again on slowly warming. (2) By proper choice of dispersion medium, it can be made practically impossible to obtain the substance in the coarse state of dispersion. (3) The most important factors governing the ability to obtain the substance in reversible dispersoid state are: the solvation, "solventolysis," dispersoid parasitism, and the ability of the medium to solidify to a gel. (4) In systems in which the solubility decreases as the temperature increases, reversible dispersoids are obtained by processes the reverse of those used for systems in which the solubility increases with rising temperature.

CHEMICAL ABSTRACTS

Precipitation of Colloids. HUMPHREY D. MURRAY (*Phil. Mag.*, 1920, [vi], **40**, 578—585).—A theoretical paper in which, from calculations based on Odén's data for colloidal sulphur and Freundlich's data for colloidal arsenious sulphide, it is shown that the minimal concentration of univalent cations required to precipitate a negatively charged colloid under similar conditions of concentration and temperature in a given time varies with the atomic number of the cation, and in general is given by an equation of the form $C=K.N^n$, in which C is the concentration of the cation, N the atomic number of the cation, n a constant for the colloid at that particular concentration, and K a constant depending on the nature of the colloid and the anion. Taking the case of univalent cations with a common anion (Cl') and sulphur as the colloid, $C_1=5\cdot9N^{-1\cdot64}$; potassium constitutes the only exception to this out of six cases examined. From a few examples, the equations $C_2=1\cdot46N^{-1\cdot64}$ and $C_3=0\cdot33N^{-1\cdot64}$ are obtained for

bivalent and tervalent cations respectively, where Cl′ is the In the case of anions with colloidal ferric hydroxide, the $C = 0{\cdot}00215N^{0{\cdot}45}$ is obtained. In all cases, when $\log C$ is p against $\log N$, straight-line curves are obtained. If the going results are substantiated, it follows that Whetham requires modification, probably by comparing the precipi power of only those ions for which the values of N^n are appr ately equal. J. F

Gelatin as an Emulsifying Agent. HARRY N. HOLMI WILLIAM C. CHILD (*J. Amer. Chem. Soc.*, 1920, **42**, 2049— —The formation of petroleum–water emulsions by the a gelatin has been studied. It is shown that the maximum ing of the surface tension should be obtained. This is se just as well by 0·3—0·4 gram of gelatin per 100 c.c. of wa by 1·0 gram. Acids, bases, and liquefying salts (sodium i sodium chloride, and sodium nitrate) also lower it a little, solidifying salts (sodium sulphate, tartrate, and citrate) ra Viscosity must not be increased more than a little beyond t water. This means either that only a small amount of gelat be used or that the gelatin must be liquefied by the proper e lytes. The latter method yields the better emulsion. An of acid, base, or liquefying salt should not be used. This pr means that the structure of the gelatin must not be en destroyed or that it must not be reduced nearly to molecula There is no convincing evidence that gelatin particles are drawn from the solution to form adhesion layers about t droplets. There is no evidence that, as the oil content is inc the gelatin content must also be increased to prodnce as g emulsion. This would certainly be the case were adhesion formed around the oil droplets. One gelatin content in a volume of water can be selected which will make the best en for all oil contents. The main factor in oil–water emulsif with the aid of gelatin is viscosity, not the maximum, b most favourable, viscosity. J. F

Determination of the Number of Independent Co uents of a System of Substances. LOUIS DUBREUIL (*rend.*, 1920, **171**, 720—721; *Bull. Soc. chim.*, 1920, [iv 809—813).—A mathematical expression is deduced which gi number of independent variables in functions of which the c in the chemical composition of a system of compounds c expressed. W

The System Na_2HPO_4–NaCl–H_2O. TSURUJI O (*J. Tokyo Chem. Soc.*, 1920, **41**, 602—620).—Primarily wi view of finding convenient transition temperatures of some h which might be used for calibrating scales between 35° a for a clinical thermometer, the author studied the effect of chloride on the transition temperature of the hydrate of di

phosphate. For the lower scale, the transition temperature 35·4° of pure $Na_2HPO_4,12H_2O \rightleftharpoons Na_2HPO_4,7H_2O + 5H_2O$ can be used. For the upper limit, 39·3° could be obtained if equal parts of the dodecahydrate and the heptahydrate of the phosphate and two-third parts of sodium chloride are mixed. More extended ranges of transition temperatures with various mixtures of the compounds and the nature of this system were studied in addition. The results obtained are given in three curves and two tables.

CHEMICAL ABSTRACTS.

Theory of the Velocity of Chemical Reaction. F. A. LINDEMANN (*Phil. Mag.*, 1920, [vi], **40**, 671—673).—A criticism of the hypothesis put forward by Lewis (T., 1918, **113**, 471). In this paper, Lewis shows that the velocity of a chemical reaction is determined by the energy density of radiation of a certain frequency. The present author points out that the radiation density may be profoundly modified by exposing the reaction to some external source of radiation, and, if Lewis's hypothesis is true, this should completely change the velocity of reaction, but no such phenomenon has been observed. Using Lewis's example for the inversion of sucrose by 0·9*N*-hydrochloric acid, it is shown that the reaction ought, on this hypothesis, to have a velocity 10^{13} times as great in sunlight as in the dark. Yet the reaction actually proceeds at appreciably the same rate whether it is exposed to sunlight or not. J. F. S.

Formula for the Temperature Dependence of Velocity Constants in Gas Reactions. J. TRESLING (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 143—148).—A mathematical paper in which the classical kinetic theory is applied, with special assumptions, to the derivation of formulæ for the dependence of reaction velocity on temperature. J. R. P.

The Velocity of Decomposition of High Explosives in a Vacuum. I. ROBERT CROSBIE FARMER (T., 1920, **117**, 1432—1445).

Rate of Chemical Action in the Crystalline State. C. N. HINSHELWOOD and E. J. BOWEN (*Phil. Mag.*, 1920, [vi], **40**, 569—578).—The rate of decomposition of potassium permanganate at 240° and 217°, solid solutions of potassium permanganate and perchlorate at 239°, ammonium dichromate at 219°, potassium permanganate and manganese dioxide at 220·5°, and tetranitroaniline at 140° and 120°, has been determined. The experiments were carried out with crystals of varying sizes, and the rate of reaction determined by the gas evolution. The change appears to be confined to those molecules in the neighbourhood of the surface, and in the region where a progressive disintegration of the crystal structure takes place the change is strongly accelerated. Solution in another solid causes a reduction in the rate of reaction. The results show that the molecules in the interior are under some kind of restraint; this may be connected with the fact

that in the interior the molecules are bound by valency forces on all sides, or it may be referred to the internal pressure.

J. F. S.

Ideal Catalysis and the Theory of Dislocation. J. Böeseken (*Rec. trav. chim.*, 1920, **39**, 623—639).—A more detailed account of work already published (compare A., 1914, ii, 554, 847).

W. G.

Promoter Action in Catalysis. Robert Norton Pease and Hugh Stott Taylor (*J. Physical Chem.*, 1920, **24**, 241—265).—Promoter action in catalysis is understood as including all those cases in which a mixture of two or more substances is capable of producing a greater catalytic effect than can be accounted for on the supposition that each acts independently and in proportion to the amount present. An example is furnished by the use of iron-molybdenum in the synthesis of ammonia. Iron and molybdenum are both catalysts for the reaction, but a mixture of equal parts of the two is much superior as a catalyst to either alone. A distinction is made between this type of activation (co-activation) and cases (activation) in which a relatively inert substance increases the activity of a catalyst. Neutral salt action is an example of the second type. Examples of promoter action in heterogeneous and homogeneous catalysis and enzyme action are given.

J. R. P.

The Constitution and Structure of the Chemical Elements. Hawksworth Collins (*Chem. News*, 1920, **121**, 219—222).—A continuation of a previous paper (this vol., ii, 680).

J. R. P.

Constitution and Structure of the Radioactive Elements. Hawksworth Collins (*Chem. News*, 1920, **121**, 243—244).—The reasoning applied in previous papers (this vol., ii, 26, 680) is extended to radioactive elements. It is concluded that the characteristic constituent of these is a portion represented by hexadic titanium. This is shown to explain the emission of β-particles from the elements.

J. R. P.

Atomic Structure and Chemical Properties. Emil Kohlweiler (*Physikal. Zeitsch.*, 1920, **21**, 543—549).—In opposition to the prevailing views on the matter, the author considers that the chemical properties of an element are intimately connected with the constitution of the atomic nucleus. The constituents of nuclei are the helium nucleus, the hydrogen nucleus, and the electron. After the building up of a central nucleus, composed of a helium nucleus, or two hydrogen nuclei, for elements of even maximum valency, the uncompensated positive charges of the helium nuclei combine to groups of eight units. The residual, ungrouped charges, varying from 0 for the inactive gases, through 8 for the transitional elements, to 14 for the halogens, then deter-

mine the chemical characters of the element. The larger or smaller number of groups of 8 positive charges corresponds with analogous elements, whilst an equal excess or deficit of positive and negative units gives rise to isotopes. The theory enables many phenomena of valency, electrochemical character, etc. (A., 1918, ii, 304), to be explained. The action of the outer electrons may mask that of the nucleus, but the assumption that the latter is of no account in determining the chemical properties is none the less incorrect. Radioactive changes are quoted as examples of changes of chemical character due to alterations of the nucleus. The impossibility of changing the chemical character of an element is compared with the independence of radioactive properties on external conditions. Changes of valency, which are readily brought about, are conditioned by the external system. The views of Kossel (A., 1916, ii, 243) are adversely criticised. J. R. P.

Stability of Atoms as Related to the Positive and Negative Electrons in their Nuclei, and the Hydrogen, Helium, H_3, H_2 Theory of Atomic Structure. WILLIAM D. HARKINS (*J. Amer. Chem. Soc.*, 1920, **42**, 1956—1997. Compare A., 1915, ii, 543, 544, 814; 1916, ii, 241; 1917, ii, 303; 1918, ii, 89; this vol., ii, 479, 541).—A theoretical paper in which the theory put forward in previous papers is extended. The negative electrons in the nuclei of atoms are largely associated in pairs, either as "binding" or "cementing" electrons. Pairs of binding electrons serve to bind together a number of positive electrons into a primary group or particle. The most abundant of these is the α-particle, consisting of 2 negative and 4 positive electrons, and having a net positive charge of 2. Its formula is $(\eta_4{}^+\beta_2{}^-)^{++}$, where η^+ is the positive and β^- the negative electron. The α-particle makes up about 90% of all known material in meteorites. A second, less abundant, group is the $(\eta_2{}^+\beta_2{}^-)^0$, or μ-group, which has a zero net charge, and makes up more than half of the rest of known material. Thus nearly all of the material, which consists of complex nuclei, exists in the form of groups made up of pairs of negative binding electrons, together with an even number of positive electrons. Isotopes of higher atomic weight differ from those of lower atomic weight by the presence of a single μ-group, or of one or two "helio"-groups, or of both a helio- and a μ-group. A helio-group consists of an α-particle with 2 negative electrons, which cement it to the nucleus of the atom. Atoms of odd net nuclear charge are relatively rare; they consist mostly of α-particles, but the odd value of the net charge is caused by the presence of one odd-numbered ν-group, $(\eta_3{}^+\beta_2{}^-)^+$, in the nucleus of each atom of odd atomic number. Of the light atoms, only glucinum and nitrogen contain an odd number of negative nuclear electrons, and these elements are not abundant. Even among the radioactive nuclei there are only a few which contain an odd number of negative electrons, and they are very unstable. The α-particle is assumed to be electrically negative in most of its

exterior, but to have a net positive charge of 2. Such particles repel one another at ordinary distances, and only attract when brought extremely close together in such a way that electrical couples are able to produce an attraction greater than the repulsion of the net charge. Neither a single positive nor a single negative electron can attach itself to such a particle, nor will two such particles unite, but three to eight, and also ten, but not more than ten, α-particles unite to form a complex nucleus, in which the mass is twice the charge and the ratio of negative to positive electrons, N/P, is 0·5. Eleven positively charged α-particles will not alone unite to form a complex nucleus, since the positive charge, 22, *is too large for the attractive action of the particles to* overcome the repulsive effect of the charge. More positive α-particles will add on if, at the same time, the ratio N/P is increased. The ratio is increased by the addition of a heliogroup, which increases the ratio N/P by a sudden jump from 0·5 to 0·55. The increased ratio makes it possible for an extra positive α-particle to attach itself, so two α-particles are added in one step and two cementing electrons in addition. Thus the cementing *electrons keep the nucleus stable as its self-repulsion increases.* The atomic weight thus increases by 8 instead of the normal 4 units. More α-particles then add on, decreasing the N/P ratio until the positive repulsion becomes so high that a second pair of cementing electrons adds on, and again the atomic weight increases with abnormal rapidity. It is shown that four series of atoms are known: the helium–thorium series, the meta-neon–uranium series, the lithium cobalt series, and the meta-chlorine series. The relationships of these series with the periodic system are discussed. The atomic weights of all pure series of atoms are very close to whole numbers when calculated on the O = 16 basis. Tables are *given of the total positive charge, total negative charge, α-cementing* electrons, excess charge, and electron contents of the nuclei of all known atoms. When the net positive charge on the nucleus of an atom becomes greater than 28, the resultant self-repulsion becomes so great that relatively few atoms of this class can be formed. Such atoms are relatively rare, and do not make up more than 1/1000 of the material of the earth and meteorites, although they constitute more than two-thirds of the elements and more than three-quarters of the atomic species. In all common atoms, the ratio N/P is 0·5, or only very slightly above this value. The atoms become rare as soon as the cementing electron content rises above 2, and no number of cementing electrons is able to stabilise a nucleus with a positive charge greater than 28. Nuclei which contain an odd number of positive electrons are rare, and those containing an odd number of negative electrons rarer still. That is, atoms with an odd nuclear charge are rare, and when they do exist they are due to an odd number of positive electrons. Nickel is undoubtedly a mixture of isotopes; it has a low mean negative electron content, and therefore has a low atomic weight for its position in the periodic system. *Nitrogen and scandium are not*

members of any of the series mentioned above. Nickel, potassium, calcium, and iodine have abnormally low nuclear contents of negative electrons, whilst argon, tellurium, barium, and selenium have high contents. Most of these elements lie near the positions of atomic weight reversal in the periodic system. There are 92 elements in the limited sense of the term, but about 300 different species of atoms. The term element is now used to denote all atoms in the nuclei of which $(P-N)$ has the same value. All elements from Ge (atomic number, 32) to Au (97) are mixtures of isotopes.

The atomic weights of the light elements are mostly whole numbers on the oxygen basis, and in the case of even atomic weights are divisible by 4, which indicates that isotopes do not occur in these elements to a large extent; exceptions are to be found in neon, chlorine, magnesium, silicon, and probably aluminium. In other cases, from atomic number 28 to 80, the whole number atomic weights correspond with the law of chance. The atomic weights of lithium and boron indicate the existence of lighter isotopes, and the hypothesis indicates that the ratio N/P should be 0·5, so the atomic weight of the lighter lithium, which is probably present to the extent of 6% in lithium, is 6, whilst that of boron is 10; an isotope of iron, 52, calcium, 44, and several of nickel, 56, 60, and 58, are all indicated. Atoms of zero atomic number may exist with masses 4, 3, 2, and 1, and possibly other values. These would contain no non-nuclear electrons, and would have no chemical and almost none of the ordinary physical properties, apart from mass.

The whole number relationship of the atomic weights when O=16 may be stated in the form that in all known complex nuclei the positive electron has the weight 1·000±0·001, whilst the free positive electron has the mass 1·007. This might be stated more accurately by giving the weight of the average electron pair, as 1·000±0·001 in any complex atom, but as 1·0077 in hydrogen itself, where the positive electron is free and not bound. The constancy in the packing effect may be a characteristic of the positive and negative electrons themselves. J. F. S.

The Possible Existence of Binding Rings in Diamond. N. H. Kolkmeijer (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 120—128).—A mathematical paper. The author agrees with Debije and Scherrer (A., 1919, ii, 20) in rejecting the binding rings of two electrons between the carbon ions in the diamond as a satisfactory explanation of the forces of valency. J. R. P.

Considerations on Certain Numerical Relations Presented by Atomic Weights. Edmond Jandrier (*Mon. Sci.*, 1920, [vi], **10**, 169—172, 194—198).—The alkali metals have atomic weights given by the formula $m7+n16$ ($n=0$ for Li); those of the alkaline earths have atomic weights given by $l9+m15+n16$. Thallium is considered an alkali metal, and bismuth a metal of the alkaline earths. The metals of the third

group have atomic weights of the form $11+m16+n17$, with the exception of gallium. Lead also follows this formula, and is considered as belonging to a branch group. Similar relations are deduced for other elements, and structural formulæ for atoms are given. J. R. P.

Binuclear Theory of Atoms and the Periodic System O. Hinsberg (*J. pr. Chem.*, 1920, [ii], **101**, 97—111).—A furthe extension of the author's theories (compare A., 1916, i, 725; 1917 ii, 173, 461; 1918, ii, 106; 1919, ii, 505). It is assumed that ther are three different arrangements of electrons within the atom: (i) nuclear electrons, which, as deduced by Fajans and Soddy fron the occurrence of isotopic elements, have no direct influence o the chemical and physical properties of elements (with the excep tion of radioactive properties), but only an indirect effect in so fa *as they neutralise the positive charges of a nucleus, and so influenc* the number of free positive charges on the atom; (ii) valenc electrons, which cause the formation of molecules by a process o neutralisation with the nuclei of other atoms; when situated a the exterior of the atoms, they are causative of the optical an chemical *properties of the latter*; (iii) ring electrons, which ar placed between two nuclei, and, according to the simplest assump tion, vibrate in a plane perpendicular to the axis of the two nuclei A distinction is drawn between reversible ring electrons (whic may pass into valency electrons by partial or complete obliteratio of *the internal ring, whereby they proceed to the neighbourhoo* of the nucleus) and irreversible ring electrons (in which thi process is impossible). They play no part in the valency questio The inactivation of a valency electron is caused by its transitio to an irreversible ring position. They are only of secondar importance for the physical, and particularly for the chemica properties of the atoms. The author illustrates his argumen by a number of examples chosen from the group of the rare eart and from the formation of simple chemical compounds. He i thus led to the conception of intra-atomic union. The formatio of molecules is a continuation of the formation of atoms; in othe words, the production of molecules is due to the neutralisation c nuclei which have been unable to complete this process within th atom. This is impossible in those cases, instanced by the ra gases, in which intra-atomic neutralisation is quantitative. Th molecules are atoms of a higher order.

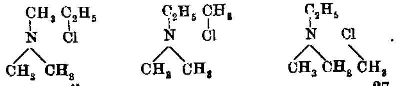
The investigation includes the consideration of the chemic properties as well as the atomic volume and boiling point of th elements. It is less exact and certain than the methods of atom physics, but provides material for this branch of the work, whic is the more valuable since considerable difficulties are encountere in the mathematical treatment of the electronic theory of ato based solely on physical data. In this connexion, a protest made against the recent dictum of Stock, that the *investigatio* of atomic structure is the province of the physicist alone.

H. W.

A New Periodic Relation between the Atomic Weights of the Chemical Elements. III. Resonance Theory of Chemical Compounds. IV. The Connexion between Rests and Magnetic Susceptibility of Atoms. KARL FEHRLE (*Physikal. Zeitsch.*, 1920, **21**, 552—555; see this vol., ii, 303).—1. The frequencies of the inactive gases calculated by the author's formula are in the ratios of simple fractions. The resonance cannot be improved by combination with other atoms, which explains the inactive character of the elements. Relations between the frequencies of atoms and molecules are discussed. 2. The form of the curve of atomic diamagnetic susceptibility is that of the differences between the experimental and ideal atomic weights ("rests"). A theory of the magnetic properties on the basis of the resonance theory is given. J. R. P.

Which Elements Form Volatile Hydrides? FRITZ PANETH (*Ber.*, 1920, **53**, [*B*], 1710—1717).—The place in the periodic system of those elements which are known to form volatile hydrides is discussed. The discovery of volatile hydrides of tin, lead, bismuth, and polonium (this vol., ii, 41, 758) makes it possible to draw a sharp line between those elements which do, and those which *do not*, form volatile hydrides. When Staigmüller's form of the periodic table is considered (A., 1902, ii, 129), in which the elements are divided into eighteen groups (the number of elements in a complete long period), it is seen that all the elements in the last four groups, including the above four elements, form volatile hydrides. Only one element not appearing in this portion of the table, boron, is known to form a volatile hydride. In other words, the four elements immediately preceding each noble gas, and boron, are the only ones which form volatile hydrides. The strange association of silicon, tin, and lead in the table is justified by the fact that they *all form volatile hydrides, apart from their metallic* or non-metallic character. The bearing of Kossel's views (this vol., ii, 681) on the volatility of the hydrides, considered from the space-lattice point of view, is discussed. E. H. R.

Subsidiary Valencies and Molecular Compounds. EDMUND NEUSSER (*Zeitsch. physikal. Chem.*, 1920, **95**, 439—440).—A theoretical paper in which it is shown that the hypothesis as to the nature of subsidiary valencies and the formation of molecular compounds put forward by Hocheder (this vol., ii, 612) leads to consequences which are not in accord with known facts. Thus, according to the hypothesis, three isomerides should be formed when ethyl chloride is added to trimethylamine. These compounds would be formulated respectively:



The sulphato- and oxalato-pentammine cobaltic salts, which are known not to be ionised in solution, must, according to Hocheder's hypothesis, be dissociated to 50% with respect to the sulphate or oxalate group. Other difficulties are quoted in connexion with *hexammine platinum chloride* and *copper thiocarbamide chloride*.

J. F. S.

Isomerism, Tautomerism, and Pseudomerism of Organic Compounds and their Relations. INGO W. D. HACKH (*Chem. News*, 1920, **121**, 85—87).—Isomerism, tautomerism, metamerism, desmotropism, and pseudomerism are caused by six factors: *N*, the number of atoms in the molecule; *K*, the kind of atom; *P*, the position or arrangement of the atoms; *T*, the chemical type of the compound; *V*, the valency of the principal atom; *L*, the linking between the atoms. The following table gives a classification of the various types of isomerism on this basis:

Organic molecules or radicles show:

	K.	*N.*	*P.*	*T.*	*V.*	*L.*	
Isology when	*d*	*s*	—	—	—	—	(structure the same)
Homology when	*s*	*d*	—	—	—	—	(,, ,,)
Polymerism when	*s*	*d*	—	—	—	—	(percentage the same)
Structure isomerism when	*s*	*s*	*d*	—	—	—	(two-dimensional)
cis-trans-Isomerism when.	*s*	*s*	*d*	—	—	—	(three-dim., inactive)
Stereoisomerism when ...	*s*	*s*	*d*	—	—	—	(three-dim., active)
Metamerism when	*s*	*s*	*d*	*d*	*s*	*s*	
Desmotropism when	*s*	*s*	*s*	*d*	*s*	*d*	
Tautomerism when.........	*s*	*s*	*d*	*d*	*s*	*d*	
Pseudomerism when	*s*	*s*	—	—	*d*	—	

where *s* = same, *d* = different, and — = same or different.

Special symbols are given to express these relationships.

J. R. P.

Method of Measuring the Rate of Flow of Gases. JOSEPH ERLICH (*Ann. Chim. anal.*, 1920, [ii], **2**, 289—297).—The apparatus described is of the type in which the upper ends of a U-shaped manometer are connected by a capillary. The gas to be measured enters by a side-tube on one limb of the manometer, passes through the capillary, and escapes through a side-tube on the other limb, the pressure caused by the passage of the gas through the capillary being registered by the change in level of the liquid in the manometer.

W. P. S.

Inorganic Chemistry.

Laboratory Apparatus for Preparing Electrolytic Hydrogen. WILLIAM GEORGE PALMER (*J. Soc. Chem. Ind.*, 1920, **39**, 316T).—A simple electrolytic cell of which the essential feature is an inverted, unglazed earthenware pot, which is covered with a parchment paper to act as a diaphragm, is described. The electrodes are of sheet nickel and the electrolyte is a 5—10% solution of potassium hydroxide. W. G.

The Crystal Lattice of the Hydrogen Haloids. A. REIS (*Zeitsch. physik.*, 1920, **1**, 299—308).—For the hydrogen haloids, the relation between ionisation energy and molecular volume does not follow the scheme given by Born for the alkali haloids (A., 1919, ii, 214). This relation for the hydrogen haloids is not reconcilable with the assumption of atomic ion lattices, but leads to the assumption of molecular lattices. Further, the inner connexion between the high ionisation energies and the low heats of sublimation of the hydrogen haloids can also only be explained on the assumption of molecular lattices. The lattice structure of the solid hydrogen haloids indicates a very marked unsymmetrical structure of the halogen ions in the molecule of the hydrogen haloids. CHEMICAL ABSTRACTS.

Action of very Concentrated Solutions of Iodic Acid on Ammonia Gas. G. DENIGÈS and J. BARLOT (*Bull. Soc. chim.*, 1920, [iv], **27**, 824—825).—It has been shown that, with solutions of iodic acid not exceeding 10% in strength, ammonia gives quadratic crystals of ammonium iodate (this vol., ii, 555). If a drop of a 50% solution of iodic acid is exposed to an atmosphere containing a trace of ammonia gas, it becomes covered with a thin white film, and if this is then well mixed with the iodic acid, rhombic crystals of ammonium tri-iodate can be observed under the microscope. If a drop of 50% iodic acid and a drop of strong ammonium hydroxide are placed a few millimetres apart on a microscope slide, the successive formation of the neutral iodate, the di-iodate, and the tri-iodate may be observed. W. G.

A New Form of Ozoniser for Laboratory Work. Y. V. RAMAIAH and M. V. N. SWAMY (*Chem. News*, 1920, **121**, 193).—The ordinary ozone tube is modified by using rarefied gas as a conductor of electricity. The tube through which the air or oxygen passes is enclosed in a glass jacket, in which the air is rarefied by a filter pump, and a second sealed tube, also connected with a filter pump, passes axially through the oxygen tube. The electrodes are small platinum disks attached to wires for the current. In a second form, the outer jacket is of aluminium. A yield of 40—50 mg. of ozone per litre with the first tube, and

50—60 mg. per litre with the second form, was obtained, using dry oxygen. J. R. P.

Distillation of a Ternary Mixture, One Constituent of which is not Volatile. PAUL PASCAL (*Bull. Soc. chim.*, 1920, [iv], **27**, 814—820).—A mathematical discussion of work already published (A., 1917, ii, 569). The results are applied to the concentration, by distillation, of nitric acids of different strength. W. G.

Hypophosphorous Acid. II. Its Reaction with Iodine. ALEC DUNCAN MITCHELL (T., 1920, **117**, 1322—1335).

The Crystalline Nature of Graphite and Temper Carbon obtained from Cast Iron. KEI IOKIBÉ (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, **9**, 275—279).—Graphite electrolytically separated from gray pig iron and temper carbon isolated from an annealed white cast iron were compressed into cylindrical rods and the diffraction figures produced by *X*-rays photographed.

Comparison with the diffraction rings of natural graphite treated in the same way showed that the photographs are identical. Hence it is concluded that temper carbon is not an amorphous substance, but differs only in fineness from natural graphite. Sugar carbon has no crystalline structure, but is an amorphous substance. An attempt to collect temper carbon from quenched carbon steels failed, as its fineness prevented separation by filtration, but since the condition of the decomposition of cementite is the same as in cast iron, the temper carbon in these steels will also be graphite. T. H. B.

Poisonous Gases from Carbon Tetrachloride Fire Extinguishers. A. C. FIELDNER, S. H. KATZ, S. P. KINNEY, and E. S. LONGFELLOW (*J. Franklin Inst.*, 1920, **190**, 543—565).—When liquid carbon tetrachloride is poured on to a fire or on to hot metal, or when the vapour is passed, together with air, through a heated iron or quartz tube, it is largely decomposed, with the formation of carbonyl chloride, free chlorine, and hydrogen chloride. At 600° the vapour decomposed much more readily in contact with iron or iron oxide than when in contact with a substance, such as quartz, chemically inert to it. Moisture promoted the formation of carbonyl chloride. At 600° none was formed in dry air in contact with quartz, but in contact with iron covered with oxide 8·3% of the chlorine of the carbon tetrachloride was converted into carbonyl chloride. The effect of iron oxide in promoting the decomposition was greater than that of water-vapour. In the experiments in the quartz tube at 800° a greater amount of the products of decomposition was formed than at 600°, whether moisture was present or not. At 800° carbonyl chloride was produced, even in dry air, in accordance with the equation $2CCl_4 + O_2 = 2COCl_2 + 2Cl_2$. The presence of turpentine vapour in the mixture of carbon tetrachloride vapour and air had an inhibiting

effect on the formation of free chlorine, but little, if any, influence on the production of carbonyl chloride. In analysing the gaseous products, chlorine was estimated by passing the gas through potassium iodide solution, and titrating the liberated iodine; whilst hydrogen chloride was estimated by aspirating the gas through alcoholic alkali hydroxide solution and titrating the total chloride formed, and deducting the amounts due to the chlorine and carbonyl chloride. For the estimation of the carbonyl chloride the gas was passed through silver nitrate on granular pumice to remove hydrogen chloride; then through antimony trisulphide on glass wool to remove chlorine; and finally through a solution of sodium hydroxide in 85% alcohol, and the sodium chloride estimated volumetrically. [See *J. Soc. Chem. Ind.*, 1920, 800A.]

C. A. M.

The Preparation and Physical Properties of Carbonyl Chloride. RALPH HALL ATKINSON, CHARLES THOMAS HEYCOCK, and SIR WILLIAM JACKSON POPE (T., 1920, **117**, 1410—1426).

The Preparation of Thiocarbonyl Chloride from Thiocarbonyl Tetrachloride. PERCY FARADAY FRANKLAND, FREDERICK HORACE GARNER, and DOROTHY WEBSTER (*J. Soc. Chem. Ind.*, 1920, **39**, 313—315T).—For the preparation of thiocarbonyl chloride by reduction of thiocarbonyl tetrachloride, tin and hydrochloric acid as reducing agent gave the best results, the yield of thiocarbonyl chloride usually being 55—60%, whilst from 20—35% of the thiocarbonyl tetrachloride was recovered. The best and most economical proportions of tin and acid to use are: 550 grams of thiocarbonyl tetrachloride, 175 grams of tin, and 500 c.c. of a mixture of equal volumes of commercial hydrochloric acid and water, the tetrachloride being added as rapidly as is consistent with efficient condensation of the distillate.

W. G.

Preparation of Pure Carbon Dioxide. ROBERT CROSBIE FARMER (T., 1920, **117**, 1446—1447).

Dilatation and Compressibility of Liquid Carbon Dioxide. C. F. JENKIN (*Proc. Roy. Soc.*, 1920, [*A*], **98**, 170—182).—The compressibility of liquid carbon dioxide was measured from $-37°$ to $+30°$ up to pressures of 100 kilos. per sq. cm. The specific volumes, coefficients of expansion, and coefficients of compressibility are given in tables and curves.

J. R. P.

A New Form of Silicic Acid. ROBERT SCHWARZ and OTTO LIEDE (*Ber.*, 1920, **53**, [*B*], 1680—1689).—By leading silicon fluoride into boiling water a form of silicic acid is precipitated, having properties which distinguish it from the product obtained by carryng out the reaction in the cold, or by the hydrolysis of silicon chloride by cold or hot water. The normal product is called α-silicic acid and the new form β-silicic acid. The β-acid, like the α-acid, when first precipitated contains about 95% of water, and

when dried over sulphuric acid about 10%. The β-acid dissolves much more slowly in hydrofluoric acid, in sodium hydroxide, or ammonia solution than the α-acid, and is scarcely coloured by methylene-blue, for which the α-acid has strong absorptive properties.

The conductivity of ammonia solutions of the β-acid was studied and compared with that of solutions of the α-acid. Expressing the quotient of the increase of conductivity occasioned by the dissolved silicic acid, Δ_ν, and the concentration, m, by Q, it is found that, under different conditions, the value of $Q \times 10^4$ for the β-acid may be 15 or 25, whilst for the α-acid it is 50 or 75. For freshly prepared, hydrated β-acid $Q=25$, and for the aged or dehydrated β-acid, $Q=15$. In the β-acid the primary particles are probably larger than in the α-acid, and the former acid in ammonia probably forms a more highly polymerised polysilicate. E. H. R.

The Effect of Various Ionogens on the Time Period Required for the Gelation of Colloidal Silicic Acid. LOUIS F. WERNER (*J. Amer. Pharm. Assoc.*, 1920, **9**, 501—508).—Acids have a very powerful peptising effect on sol colloidal silicic acid. In the case of the strong acids this effect is most marked at medium concentrations. Alkalis also have a strong peptising influence; the effect is greatest at medium to low concentrations for the highly ionised bases, and in the case of the slightly ionised bases the effect is great in all but the lowest concentrations tried. Salts have no effect in presence of acids, but in presence of bases the congealing effect is hastened. The potassium salts of several negative radicles decreased the time required for gelation. The chlorides of various metals, with the exception of ferric and cupric chlorides, decreased the time of gelation. Disodium and monosodium phosphates have strong congealing powers, but trisodium phosphate has the opposite effect. Di- and tri-sodium citrates accelerate the setting greatly, the effect decreasing with the concentration, but in the case of the monosodium salt the time for setting is the same for all concentrations. The acetates of the various metals have the greatest congealing effect (excepting mercury). Inorganic salts produce but little effect. The alkali salts of the organic acids produce powerful accelerating effects, except the carbonates and hydrogen carbonates, which have a peptising effect in medium to dilute solutions. CHEMICAL ABSTRACTS.

Constitution of the Silicates. JOHANN JAKOB (*Helv. Chim. Acta*, 1920, **3**, 669—704).—The author discusses the general principles underlying the structure of the silicates and develops systematically the formulæ of silicates of the most varied type, starting with the simplest and proceeding to those of gradually increasing complexity. The nomenclature of the different compounds is likewise considered.

The classes into which the silicates are divided are as follows: I. Silicates with simple silicic acid ions: (1) Hexaoxy-silicates, such

as asperolith, $\left[SiO_6\right]{Cu \atop H_6}$, $\left[SiO_6\right]{Al_2 \atop Mg(Fe)}$, dumortierite, $[SiO_6]_3Al_8$. (2) Pentaoxy-silicates, such as andalusite, $[SiO_5]Al_2$, titanite, $\left[SiO_5\right]{Ca(Fe) \atop Ti}$. (3) Tetraoxy-silicates ("orthosilicates"), such as dioptase, $\left[SiO_4\right]{Cu \atop H_2}$. II. Silicates with complex silicic acid ions: (1) Monosilicohexaoxysilicates, such as serpentine,

$$\left[SiO_2\ SiO_6\right]{Mg_3 \atop H_2,OH_2}.$$

(2) Disilicohexaoxysilicates, such as meerschaum,

$$\left[{SiO_2 \atop SiO_2}\ SiO_6\right]{Mg_2 \atop H_4}+xH_2O.$$

(3) Trisilicohexaoxysilicates, such as the pyroxenes and many of their products of hydrolysis, for instance, talc, $\left[Si\left({O \atop O}Si{O \atop O}\right)_3\right]{Mg_3 \atop H_2}$. (4) More highly silicated hexaoxysilicates, as yet unknown. III. Silicato-salts: (1) Tetraoxysilicato-salts, such as nepheline,

$$\left[Al\left({O \atop O}Si{O \atop O}\right)_3\right]{Al_2 \atop Na_3}.$$

(2) Pentaoxysilicato-salts, of which sillimanite, $[Al(SiO_5)_3]Al_5$, possibly represents the type. (3) *Hexaoxysilicato-salts*, for example, dumortierite, $[SiO_6]_4Al_8$. (4) Trisilicotetraoxysilicato-salts of the type $[Al(SiO_4\ SiO_2)_3]R_9$, such as leucite,

$$\left[Al(SiO_4\ SiO_2)_3\right]{Al_2 \atop K_3(Na)}.$$

(5) Hexasilicotetraoxysilicato-salts, such as orthoclase,

$$\left[Al(SiO_4\ SiO_2\ SiO_2)_3\right]{Al_2 \atop K_3}.$$

(6) Trisilicopentaoxysilicato-salts, to which rasonite,

$$\left[Pb(SiO_5\ SiO_2)_3\right]\begin{matrix}Pb_5\\Ca_3\\CaCl_2\end{matrix},$$

and ganomalite, $\left[Pb(SiO_5\ SiO_2)_3\right]\begin{matrix}Pb_5\\Ca_3\\Ca(OH)_2\end{matrix}$, probably belong. (7) Hexasilicopentaoxysilicato-salts, such as pollux,

$$\left[Al(SiO_5\ SiO_2\ SiO_2)_3\right]\begin{matrix}Al_3\\Cs_4\\H_2\end{matrix}.$$

(8) Trisilicohexaoxysilicato-salts, such as *olivine*,

$$[Mg(SiO_6\ SiO_2)_3](Mg,Fe)_{11}.$$

(9) More highly silicated silicato-salts, $[Al(SiO_6\ SiO_2\ SiO_2)_3]R_{21}$, as yet unknown. IV. Co-ordination compounds of the highest order, in which, not an atom, but an atomic grouping, appears as coordination centre; to this class belongs tourmaline (Reiner, A., 1913, ii, 718; Wülfing and Becht, A., 1914, ii, 63).

Many types of these silicate compounds are able to crystallise both with and without water of crystallisation; this deposition of water molecules is fundamentally a partial regeneration of complex hydrate ions, such regeneration rendering possible subsequent dissociation or hydrolysis. T. H. P.

Application of a New Physico-chemical Volumetric Method. René Dubrisay (*Compt. rend.*, 1920, **171**, 670—672). —Applying the method previously described (A., 1919, i, 73; ii, 78) to the study of the neutralisation of sulphuric acid, the author finds a point of inflexion on the curve corresponding with the formation of sodium hydrogen sulphate and another at the point where the normal salt is obtained.

With solutions of sodium sulphate and sulphuric acid the difference between the observed and calculated temperatures reaches a maximum when the solutions are mixed in equimolecular proportions. The same holds good for solutions of sodium sulphate and hydrochloric acid. W. G.

Crystal Structure of Sodium Nitrate. Ralph W. G Wyckoff (*Physical Rev.*, 1920, **16**, 149—157).—Laue photographs were taken through crystals of sodium nitrate normal and slightly inclined to the (111) and (100) face. It is found, using a method of interpretation similar to that of Nishikawa, that the crystal can be referred to a set of interpenetrating rhombohedral lattices with axes which are the diagonals of the plane formed by taking the usual crystallographic axes as edges. The lattice arrangement thus found is that anticipated by Bragg on the basis of partial measurements, and is essentially the same as that of calcium carbonate, that is, may be regarded as similar to that of sodium chloride with NO_3 groups replacing the chlorine atoms. The co-ordinates of the atoms, assuming the length of the sides of the unit rhombohedron to be 1, are sodium at (0, 0, 0), and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$); nitrogen at ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) and ($\frac{3}{4}$, $\frac{3}{4}$, $\frac{3}{4}$); oxygen at (β, 1—β, 0); (0, β, 1—β); (1—β, 0, β); ($\frac{1}{2}$—β, β—$\frac{1}{2}$, $\frac{1}{2}$); (β—$\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$—β); ($\frac{1}{2}$, $\frac{1}{2}$—β, β—$\frac{1}{2}$), where β is very nearly $\frac{1}{4}$. Chemical Abstracts.

The Production of Ammonium Sulphate from Coke-oven Gases by the Feld Process. F. Raschig (*Zeitsch. angew. Chem.*, 1920, **33**, 260—262).—By the Feld process (A., 1912, ii, 448) both hydrogen sulphide and ammonia are recoverable from coke-oven gases with production of ammonium sulphate. The operations comprise treatment of the gases with aqueous solutions of ammonium trithionate and tetrathionate, recovery of these from the thiosulphate formed by the action of sulphur dioxide, and their decomposition on boiling into ammonium sulphate, sulphur dioxide, and sulphur, followed by oxidation of the sulphur. In regard to the reaction $4(NH_4)_2S_2O_3 + 6SO_2 = 2(NH_4)_2S_3O_6 + 2(NH_4)_2S_4O_6$, examination of the behaviour of analogous sodium compounds shows that with dilute solutions, only sulphite and

sulphate with traces of polythionates are formed. If the solution is very concentrated, the conversion into the polythionates proceeds rapidly. During an investigation of the polythionates it was discovered that by interaction with sodium sulphite, penta- and tetrathionate are converted into trithionate and thiosulphate: $Na_2S_5O_6 + 2Na_2SO_3 = Na_2S_3O_6 + 2Na_2S_2O_3$ and $Na_2S_4O_6 + Na_2SO_3 = Na_2S_3O_6 + Na_2S_2O_3$; treatment of the trithionate with sulphite fails to yield dithionate, which is therefore not a true polythionate. The decomposition of acid solutions of thiosulphates into sulphurous acid and sulphur is not quantitative, and is accompanied by the formation of pentathionate owing to polymerisation of the thiosulphate. This effect is increased by addition of a trace of an alkali arsenite as a catalyst. In practice, the treatment of the thiosulphate with sulphur dioxide may therefore be represented by the equations:

$$(1)\ 5Na_2S_2O_3 + 3SO_2 = 2Na_2S_5O_6 + 3Na_2SO_3.$$

$$(2)\ 2Na_2S_5O_6 + 3Na_2SO_3 = Na_2S_3O_6 + Na_2S_4O_6 + 3Na_2S_2O_3,$$

and this gives the reaction stated by Feld:

$$2Na_2S_2O_3 + 3SO_2 = Na_2S_3O_6 + Na_2S_4O_6.$$

The reactions have been based on proportions of ammonia and hydrogen sulphide of 2:1. With excess of ammonia the recovery of the thionates is retarded, and more hydrogen sulphide must be introduced into the gases. A preponderance of hydrogen sulphide necessitates partial oxidation to sulphur. W. J. W.

The Melting and Boiling Points of Ammonium Sulphate. E. Jänecke (*Zeitsch. angew. Chem.*, 1920, **33**, 278—280).—The equilibrium relations between sulphuric acid, ammonia, and acid and normal ammonium sulphates have been investigated, and the results obtained have been plotted on curves. At atmospheric pressure it is shown that the hydrogen sulphate, $(NH_4)HSO_4$, has m. p. 251° and b. p. 490°, and the normal sulphate, $(NH_4)_2SO_4$, has the same m. p. and b. p. 357°. The eutectic mixture has m. p. 195°. The author pleads for more investigations of the physical properties of the common chemicals in everyday use. A. J. H.

Fusion of Zinc, Cadmium, and Mercury Sulphides. Erich Tiede and Arthur Schleede (*Ber.*, 1920, **53**, [*B*], 1717—1721).—These sulphides, which sublime without melting under atmospheric pressure, have been obtained in the molten condition by heating in a carbon-tube pressure furnace in an atmosphere of nitrogen. Zinc sulphide melted under 100—105 atm. at 1800—1900°. The solidified fused sulphide had a lustrous appearance and a bright greenish-yellow colour; it proved to be the hexagonal modification. Cadmium sulphide was fused at 100 atm. at about 1750°; the fused solid had a dark brownish-yellow colour and lustrous appearance. Mercuric sulphide was fused at 120 atm. and 1450°. The fused solid had a steel-grey, matt appearance, and, when rubbed, quickly became red. E. H. R.

Thermochemical Analyses of Solutions. E. Chauvenet, P. Job, and G. Urbain (*Compt. rend.*, 1920, **171**, 855—857).—The

method used is similar to that described by Dubrisay (this vol., ii, 508), and by its use the existence of the double salts $2KI,CdI_2$; $2CuCl_2,3MgCl_2$; $3CuCl_2,2MgCl_2$; $2CuCl_2,3CaCl_2$; $CuCl_2,CaCl_2$; $CuCl_2,2AlCl_3$ and $2CuCl_2,AlCl_3$ is shown. W. G.

Lead Hydride. FRITZ PANETH and OTTO NÖRRING (*Ber.*, 1920, **53**, [*B*], 1693—1710).—The methods previously employed for the detection of the hydrides of bismuth (A., 1919, ii, 67, 68) and tin (this vol., ii, 41) have been applied in the study of the possibility of the existence of a hydride of lead. Magnesium powder was activated with thorium-*B* and thorium-*C* in a desiccator for half-an-hour and was then dissolved in 0·1 or 0·2*N*-hydrochloric acid, the resulting gases being carried in a stream of hydrogen through a cotton-wool filter to a heated Marsh tube. The radioactivity of the metallic deposit, consisting chiefly of thorium-*C* (bismuth), was then examined. For the first few hours its behaviour was indistinguishable from that of thorium-*C*, but after twenty-four hours, by which time the thorium-*C* should have disappeared, a notable activity remained, the rate of disappearance of which corresponded with that of thorium-*B* (lead). The "yield" of lead obtained, however, was only about one hundredth that of the bismuth. The lead hydride appeared to be stopped or decomposed more readily by a thick cotton-wool filter than bismuth hydride.

Attempts to prepare the hydride by the action of acids on ordinary lead–magnesium alloys were unsuccessful, and so were numerous attempts by electric methods, for example, induction sparks or an arc in an atmosphere of hydrogen. Success was eventually attained by a combined electrolysis-spark process in a specially designed apparatus. Using dilute sulphuric acid as electrolyte and a lead–glycerol cement cathode, with an *E.M.F.* of 220 volts, the apparatus was so arranged that intermittent sparking at high frequency occurred between the cathode and the electrolyte. The cathode gases were passed to a condensing tube immersed in liquid air where any lead dust was deposited, whilst the hydride was liquefied. On allowing the temperature to rise, the hydride was again vapourised and passed through a cotton-wool filter to a heated Marsh tube, where it was decomposed and lead deposited. The deposit had a dull grey colour, and was close to the flame, but not so close as a tin deposit. The lead was identified by a number of chemical tests which distinguished it from arsenic, antimony, tin, tellurium, or bismuth. A number of modifications of the experiment indicated that the hydrogen required for the formation of the hydride is not derived from the electrolysis of the electrolyte, but probably through the action of the spark, positive hydrogen ions combining directly with negative lead ions. So-called active hydrogen may play a part in the reaction. E. H. R.

Combinations of Haloid Derivatives of Lead and Thallium. BARLOT (*Compt. rend.*, 1920, **171**, 794—796).—Conductivity measurements show the existence of double *chlorides*,

bromides and *iodides* of lead and thallium having the general formula TlX,PbX_2, and the author has obtained all of these in a crystalline form. There are indications of the existence of a second double chloride, $2TlCl,PbCl_2$, but this could not be isolated. W. G.

Thermal Analysis of the System Thallium Nitrate: Thallium Nitrite. VITTORIO CUTTICA (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 89—92. Compare Rolla and Belladen, this vol., ii, 34).—The thermal behaviour of fused mixtures of thallium nitrate and nitrite excludes the formation of complexes. The two salts form an uninterrupted series of mixed crystals, the transformation in the solid state corresponding with Roozeboom's type II.

T. H. P.

Study of the Transformation Points by a Dilatometric Method. PAUL BRAESCO (*Ann. Physique*, 1920, [ix], **14**, 5—75). —The first part of the paper is a detailed account of work already published (A., 1919, ii, 153). The method has been applied to the study of alloys and by means of it the author has proved the existence of the definite copper-antimony compound Cu_3Sb. With copper-aluminium alloys, the phenomena of tempering are particularly well shown by this method. In the case of the bronzes, the allotropic transformation of the compound Cu_4Sn was observed and also the transformation $\beta \rightarrow \alpha + \delta$. W. G.

Determination of the Atomic Weight of Thulium. C. JAMES and O. J. STEWART (*J. Amer. Chem. Soc.*, 1920, **42**, 2022—2023).—The atomic weight of thulium has been determined from the ratio $TmCl_3 : 3Ag$ from three specimens of thulium obtained as described previously (A., 1911, ii, 891). The experimental procedure was identical with that followed in the determination of the atomic weight of samarium (A., 1918, ii, 44). The purest fraction gave a value 169·44 for the atomic weight as a mean of three determinations, whilst the other two fractions, which contained neoytterbium, gave 169·66 and 169·90 respectively.

J. F. S.

Sodium Aluminates. Equilibria in the System Na_2O-Al_2O_3-H_2O. F. GOUDRIAAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 129—142).—At 30°, two stable aluminates occur in the system Na_2O–Al_2O_3–H_2O, namely,

$$4Na_2O,3Al_2O_3,16H_2O \text{ and } 4Na_2O,Al_2O_3,10H_2O.$$

Both form incongruently saturated solutions, that is, are decomposed by water and dilute sodium hydroxide solution. According to the mode of preparation, aluminium hydroxide may be obtained in different forms. Under special conditions, alumina forms a crystalline hydrate, $Al_2O_3,3H_2O$. The gelatinous hydroxide must be considered as a metastable phase of variable composition. It adsorbs variable quantities of alkali. There is very probably a continuous transition between these gelatinous hydroxides and the crystalline hydrate. Aluminium oxide is metastable at 30° in

respect of the hydrate. The swelling exhibited by the desiccated particles of hydroxide and oxide is dependent on the alkalinity of the solution. J. R. P.

The Equilibrium-diagram of Carbon–Manganese Alloys K. KIDO (*Sci. Rep. Tôhoku. Imp. Univ.*, 1920, **9**, [iv], 305—310) —The object of this investigation was to establish the equilibrium diagram of manganese and carbon with a high degree of certainty. A series of alloys was prepared by diluting with manganese the carbide Mn_3C, made in an electric furnace. In the liquid state the carbide and manganese are soluble in all proportions, bu only partly in the solid state. The saturation points of carbid in manganese and manganese in carbide were determined. A the temperature falls, the solubility of both decreases, and the form a eutectoid having a composition of about 3·7% C. Specimen quenched at different temperatures and subjected to micro examination showed that the eutectoid temperature is a littl above 900°, and the transformation takes place at a somewha lower temperature during cooling than on heating. Therma analysis confirmed this, showing an absorption of heat above 90(during heating and an evolution of heat at about 830° on coolin T. H. B.

The Point Ar_3 of Steels, and Martensite. P. DEJE (*Compt. rend.*, 1920, **171**, 791—794).—A review of his previo work (compare A., 1917, ii, 477) in the light of recent work I Guillet (*Rev. gén. Sci.*, 1920, **31**, 496). W. G.

Metal Tubes which are Stable towards Water Vapo at Temperatures above 1000°. PAUL ASKENASY (*Zeits Elektrochem.*, 1920, **26**, 436).—Tubes made from silicised ir sheet are very little attacked by air, or mixtures of steam a oxygen at temperatures of 1100°. The metal is brittle, but careful heating may be raised to a red heat and can then be be into a tube which can be welded by the autogenous method. Su tubes, when surrounded by cast iron, serve well as superheat for steam. Chromium nickel tubes are equally resistant to ste at high temperatures. J. F. S

Hydrous Oxides. I. and II. HARRY B. WEISER (*J. Physi Chem.*, 1920, **42**, 277—328, 505—538).—1. HYDROUS FER OXIDE.—A survey of investigations on the composition of colloi ferric oxide has been made. The existence of no definite b ferric salt has been established with certainty, and only one defi crystalline hydrate has been prepared. The latter is formed o under special conditions, namely, the decomposition of sodi ferrite by water at the ordinary temperature. It is prob that the different ferric iron colloids are not composed of b salts of varying composition or of hydrous hydrated oxides, are hydrous ferric oxide. The difference in properties of collo

ıydrous ferric oxides prepared by different methods and of lifferent ages is due to a difference in the degree of hydration .nd in the size of the colloidal particles. It is unnecessary to ostulate the existence of basic chlorides or complex salts of varyng composition in order to account for the existence of only a art of the chlorine in the dialysed Graham colloid as the hloride ion.

Certain electrolytes precipitate the Péan de St. Gilles colloid n a gelatinous form, whilst others precipitate it in a granular orm. The nature of the precipitate depends on the conditions f precipitation; the same electrolyte may produce either a ranular or gelatinous mass in suitable circumstances. The most elatinous precipitate is obtained when there is very rapid aggreation of the hydrous particles throughout the entire solution nd when the electrolyte present exerts no solvent action; the ost granular precipitate results when the agglomeration proceeds lowly and when the electrolyte possesses a solvent action.

The influence of the valencies of the ions of the precipitating lectrolytes was investigated.

Hydrochloric acid has two precipitating values for the Péan e St. Gilles colloid, one above the other with a zone of non-preipitation between, in which the colloid is less stable than the riginal colloid. The degree of reversibility of the precipitation f hydrous ferric oxide is determined mostly by the specific dsorbability of the precipitating ion, although the physical haracter of the precipitate has an influence.

It is not probable that the different colours of hydrous ferric xide (reddish-brown, yellow, and red) are due to complex salts r hydrous hydrated oxides, since it is possible to make a transiion from brown to yellow by increasing the size of the particles. 'his may be effected by heating water to which ferric chloride as been added. The yellow colloidal hydrous oxide is not readily ehydrated at 100° and probably contains adsorbed ferric salt.

A yellow colloidal solution was prepared by the Péan de St. illes method by allowing the acetate solution to remain for a few ays before diluting and boiling. The slow hydrolysis of the cetate favours the formation of yellow hydrous oxide stabilised y adsorbed ferric salt. When the solution is boiled, a stable ellow colloid is formed instead of the usual brick-red.

II. Hydrous Aluminium Oxide.—Aluminium oxide forms only ne definite hydrate, the trihydrate, precipitated from solutions the oxide in alkali. The so-called hydrates formed by prepitating with ammonia are hydrous oxides. Any number of ydrous oxides, similar to those of ferric oxide, may be prepared, ffering in size of particles and amount of water. The larger and ss hydrous the particles, the less soluble are they in acids and kalis. There is no temperature of inversion from soluble oxide insoluble meta-oxide. The colloidal oxide prepared by prouged digestion of aluminium acetate at high temperature is soluble in acids and alkalis and has no mordanting action; the

colloid prepared by peptising gelatinous alumina with aluminium chloride and dialysing in the cold is soluble in acids and alkalis and possesses a mordanting action. Colloids with intermediate properties may be obtained.

Colloidal alumina is a positive colloid and is stabilised by preferential adsorption of cations. The relative peptising power at 100° was found to be in the order: nitric acid>hydrochloric acid>ferric chloride>aluminium chloride>acetic acid. It is probably incorrect to assume the formation of aluminium ion as an intermediate step in the peptisation of aluminium oxide by acids and salts. The colloids formed by peptisation of gelatinous alumina are not composed of basic salts of varying composition, neither is there any necessity to assume the formation of a series of hypothetical complex salts to account for the properties of the colloid.

The coagulation of colloidal aluminas by electrolytes was studied. Strong acids with univalent anions and their salts precipitate the colloid only at high concentrations and the reaction is reversible. Acids with multivalent anions and their salts precipitate the colloid at low concentrations and irreversibly. Rose's explanation of the cause of the reversibility of precipitation is shown to be untenable. Gelatinous alumina dissolves in sodium or potassium hydroxide with the production of an unstable aluminate, from which colloidal hydrated alumina separates in a granular, sparingly soluble form. Observation of the effect of the nature of the coagulating agent on the physical character of the precipitated oxide confirmed the conclusions reached with ferric oxide.

J. R. P.

The Double Colloidal Sulphide of Iron and Sodium. S. M. Horsch (*Bull. Soc. chim.*, 1920, [iv], **27**, 777—779).—When hydrogen sulphide is passed over a molten mixture of sodium hydroxide and ferric oxide, a double sulphide, $FeS,4Na_2S$, is obtained, which dissolves in water, giving a deep emerald-green solution. Its aqueous solution, after dialysis, in the absence of air, retains the two sulphides in the proportion given. A concentrated solution on cooling gives a hydrogel, having the composition $Na_2S,2FeS$, which dissolves in water, giving a black solution, and on adding ammonium chloride to this solution, ferrous sulphide is precipitated. If to this solution the requisite amount of sodium sulphide is added, it regains the original green colour.

W. G.

The Stability of the Cobaltammines. Arthur B. Lami and Alfred T. Larson (*J. Amer. Chem. Soc.*, 1920, **42** 2024—2046).—The six cobaltammines examined were aquopentamminecobalt chloride, diaquotetramminecobalt chloride 1 : 2-dinitrotetramminecobalt chloride, nitropentamminecobalt chloride, hexamminecobalt chloride, and 1 : 6-dinitrotetrammine cobalt chloride. The oxidation potentials of aqueous solution of these ammines in 3·265*M*-ammonium hydroxide solution wer

measured, and from these results the concentrations of the simple cobaltic ions in these solutions were calculated, thus giving a measure of the relative stability of the ammines. They are arranged above in order of descending stability.

The potentials of the cobalt–cobaltous electrode in cobaltic chloride solution and in ammoniacal cobaltic chloride solutions were measured, and from these results the formula of the amminocobaltous ion in the presence of excess of ammonia is shown to be $Co(NH_3)_6^{\cdot\cdot}$. The equilibrium constant for its dissociation into ammonia and simple cobaltous ions has been calculated.

The value for the cobaltous–cobaltic potential, as redetermined, is 1·775 volts at 0° with a temperature-coefficient of +0·00169 volt.

W. G.

Influence of Chromium Compounds on the Corrosion of Iron. George W. Heise and Amando Clemente (*Philippine J. Sci.*, 1920, **16**, 439—446).—Passivifying agents, such as potassium dichromate, may increase the corrosion of iron in salt solutions, owing to formation of free acid, and the depolarising effect of the dichromate: $H_2O + K_2Cr_2O_7 + 2NaCl \rightleftharpoons K_2CrO_4 + Na_2CrO_4 + 2HCl$. Experiments were carried out to determine the influence on corrosion produced by increasing amounts of potassium dichromate added to sulphuric acid of various strengths. With $N/2$-sulphuric acid corrosion was accelerated proportionately to the amount of dichromate added up to a concentration of above 19 grams, at which stage the iron became passive; with further additions of dichromate corrosion gradually diminished. With N-acid the passive condition was more indefinite, but was reached in individual cases with a concentration of 50 grams per litre. Increase of corrosion up to this point, and decrease beyond it, occurred as with $N/2$-acid. In the case of $2N$-acid no passive state was reached even when a saturated solution of dichromate was employed, and corrosion was accelerated by the addition of increasing amounts of the salt.

The addition of a small amount of potassium dichromate and potassium chromate to 10% sulphuric acid at first increased the corrosion of iron, but after reduction of the salt had taken place no further effect occurred with increased time of treatment. Chromium sulphate or chloride is apparently without influence on the rate of corrosion, the results obtained by Watts (*Trans. Amer. Electrochem. Soc.*, 1912, **21**, 337—353) not being confirmed. Differences in the iron used and in the acid concentration may account for this divergence.

W. J. W.

The Precipitation of Tin by Iron. I. M. Kolthoff (*Rec. trav. chim.*, 1920, **39**, 606—608).—A reply to Bouman (this vol., ii, 547).

W. G.

The Solubility of Earth-acid Gels [Titanic, Tantalic, and Columbic Acids] in Hydrogen Peroxide–Acid Mixtures. Otto Hahn and Hans Gille (*Zeitsch. anorg. Chem.*, 1920, **112**, 283—292).—For the separation of titanic, tantalic, and columbic

acids from most other elements, a method was given by Weiss an Landecker (A., 1909, ii, 942) which consisted in dissolving the acid whether precipitated from acid or basic solutions, in hydrogen pe oxide and reprecipitating by boiling the solution with sulphurou acid. Experiments on the solubility of these acids in acid solution of hydrogen peroxide have not confirmed Weiss and Landecker statements. The acids used for the experiments were prepared b fusing the commercial material with sodium hydrogen sulphat extracting with boiling water, and hydrolysing the solutions b boiling with sulphurous acid. Titanic and columbic acids are pra tically completely soluble in acid hydrogen peroxide, but tantal acid when precipitated hot is almost insoluble, and when precip tated cold is only partly soluble. In mixtures, the different aci influence one another differently according to the conditions. Ta talic acid lowers the solubility of columbic acid, whilst titanic ac may increase the solubility of tantalic acid or may itself be render less soluble. Experiments with the ultra-microscope indicate tha in acid hydrogen peroxide solutions, titanic acid forms a tr solution, whilst columbic and tantalic acids form colloidal solutio

E. H. R.

Colloidal Sulphur Compounds of Ruthenium. F. JAEGER and J. H. DE BOER (*Proc. K. Akad. Wetensch. Amsterda* 1920, **23**, 95—102).—The product of the precipitation of a salt quadrivalent ruthenium by ammonium sulphide differs with t temperature. At 100° brownish-black RuS_2 is formed, togeth with free sulphur, but at 0° greenish-black RuS_6 is formed, whi has the character of an irreversible colloid and with excess ammonium sulphide gives a green, unstable colloidal solution. intermediate temperatures mixtures of both sulphides and f sulphur are formed. The dark green sulphide and the green c loidal solution of RuS_6 (containing positively charged partic rapidly absorb free oxygen, forming a reddish-violet solution the reversible colloid ruthenium pyrosulphite, RuS_4O_{10}, the partic of which are positively charged. This salt is in turn converted oxygen (air, nitric acid, permanganate) into ruthenium sulph and free sulphuric acid. The properties and reactions of products were investigated.

J. R. P

Mineralogical Chemistry.

The Nomenclature and Classification of Sulph Minerals. EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 19 **10**, 487—496).—A tabular classification is given on much the sa lines as that of Dana's "System of Mineralogy" (6th edit., 18

but in greater detail. Several incompletely described minerals are listed. In addition to selenides, tellurides, arsenides, antimonides, and bismuthides, there are also included the few naturally occurring oxysulphides, nitrides, phosphides, carbides, and silicides.

L. J. S.

Composition of Minerals of the Hydrotalcite Group. WILLIAM F. FOSHAG (*Proc. U.S. Nat. Mus.*, 1920, **58**, 147—153).—Hydrotalcite from Kongsberg, Norway, consisting of curved lamellar masses with white colour and pearly lustre, gave anal. I, agreeing with $6MgO,Al_2O_3,CO_2,12H_2O$ or

$$MgCO_3,5Mg(OH)_2,2Al(OH)_3,4H_2O.$$

This mineral is thus a basic carbonate rather than a hydrated oxide, as previously regarded. It glows intensely before a blowpipe, becoming silvery-white, but does not fuse. Stichtite (of W. F. Petterd, 1910 = Chrom-brugnatellite of L. Hezner, A., 1912, ii, 1061) from the original locality in Tasmania, gave II, agreeing with the analogous formula $6MgO,R_2O_3,CO_2,12H_2O$. Before the blowpipe it glows intensely, turns light grey, and becomes magnetic, but does not fuse.

	SiO_2.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	CO_2.	H_2O.	Total.
I.	0·44	15·32	—	1·89	0·28	nil	39·72	7·60	35·46	100·71
II.	2·09	2·24	14·08	4·04	0·28	trace.	36·59	6·94	33·01	99·27

Previous analyses of pyroaurite suggest that the formula for this should be $6MgO,Fe_2O_3,CO_3,12H_2O$. A new estimation of ferrous iron in pyroaurite from Långban, Sweden, gave FeO 0·74%. These minerals all possess a perfect basal cleavage, and are optically uniaxial with weak birefringence. Brugnatellite (A., 1909, ii, 247) probably belongs to the same group, and may be identical with pyroaurite. Hydrotalcite, stichtite, and pyroaurite result from the alteration of corresponding members of the spinel group, namely, spinel, chromite, and jacobsite respectively.

L. J. S.

Vonsenite, a New Mineral. ARTHUR S. EAKLE (*Amer. Min.*, 1920, **5**, 141—143).—A large boulder-shaped mass of a coal-black mineral with brilliant, metallic lustre occurs with magnetite, chlorite, and pyroxene at a granite limestone contact at Riverside, California. It is quite opaque and non-magnetic; H 5, D 4·21. Imperfect, prismatic crystals are orthorhombic or monoclinic ($a:b =$ 0·7558). The mineral fuses at 3 to a black, magnetic bead, and it is completely soluble in hydrochloric or sulphuric acid. The average composition is:

FeO.	MgO.	B_2O_3.	Fe_2O_3.	Total.
39·75	10·71	14·12	34·82	99·40

Other estimations of magnesia gave 7·43—11·51%. These results agree with the ludwigite formula, $3(Fe,Mg)O,B_2O_3+FeO,Fe_2O_3$, but with ferrous oxide largely in excess of magnesia. Further, the mineral differs structurally and optically from ludwigite. L. J. S.

Higginsite, a New Mineral of the Olivenite Group. CHARLES PALACHE and EARL V. SHANNON (*Amer. Min.*, 1920, 5 155—157).—Occurs as bright green, orthorhombic crystals ($a:b:c=0.6242:1:0.7940$) in black manganese ores at the Higgin mine, Bisbee, Arizona. H $4\frac{1}{2}$, D 4·33, fusibility 3; readily soluble in hydrochloric or nitric acid, partly soluble in sulphuric acid, and insoluble in ammonia. Analysis gives the formula

$$2CuO,2CaO,As_2O_5,H_2O$$

or $CuCa(OH)(AsO_4)$, analogous to those of olivenite and descloizite

CuO.	CaO.	V_2O_5.	As_2O_5.	H_2O < 105°.	H_2O > 105°.	Fe_2O_3.	MnO.	Insol.	Total.
28·67	20·83	1·97	41·23	0·08	3·41	0·48	2·84	0·86	100·37

L. J. S.

Australian Minerals. C. ANDERSON (*Rec. Australian Museum* 1920, **30**, 1—31).—Detailed crystallographic descriptions are given of several mineral species from various Australian localities; analyses are given of the following: Corroded crystals of beryl (aquamarine), from Torrington, N.S.W., have low D 2·664 and refractive indices $\omega=1.5685$, $\epsilon=1.5640$ (Na), and are correspondingly poor in alkalis, as shown by the following analyses by J. C. H. MINGAYE (*Ann. Rep. Dept. Mines, N.S.W.*, 1916, for 1915, 198):

	SiO_2.	Al_2O_3.	GlO.	FeO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.	Sp. g
I.	66·08	19·86	12·96	0·30	nil	0·43	nil	0·58	100·21	2·66
II.	64·70	22·22	11·84	0·37	0·04	0·24	0·13	0·60	100·14	2·66

Also traces of Mn, Li, Sr, and Cs (?); absence of Ca, Cr, V, Associated with the beryl is wolframite, which, containing on 3·95% MnO, is near the ferberite end of the series. Chabazite (var. phacolite), as small crystals with calcite in decomposed basalt near Glen Innes, N.S.W., gave SiO_2 45·71, H_2O 21·91%. Mimetite, almost white crystals in limonite, from Mount Bonnie, Northern Territory, gave:

PbO.	As_2O_5.	P_2O_5.	Cl.	Total (less O for Cl)
76·22	20·55	1·41	2·00	99·73

L. J. S.

Analytical Chemistry.

A Graduated Tap Funnel for the Acid Incineration Mixture in Neumann's Method. GEORG LOCKEMANN (*Zeit. physiol. Chem.*, 1919, **107**, 211—212).—The manipulation of Neumann's wet method for ashing organic substances (A., 1 ii, 243; 1905, ii, 68) is facilitated by the use of a graduated funnel for running in the acid mixture. S. S.

Use of Ultrafiltration in Toxicological Analysis. C. Mannich and Grete Wipperling (*Ber. Deut. pharm. Ges.*, 1920, **30**, 348—361).—Ultrafiltration (filtration through collodion membrane) is not suitable generally for toxicological work, owing to loss of alkaloids and heavy metals, due to absorption of these by the membrane. The loss is small, but it is important when dealing with traces of poisons; it is greatest in the case of mercury and practically negligible for arsenic and antimony. The method, however, is useful for the separation of potassium chlorate and oxalic acid from organic substances, etc. W. P. S.

Alignment Chart for Reduction of Gaseous Volumes. Hans G. Schwerdt and W. W. Loebe (*Chem. Zeit.*, 1920, **44**, 818—819).—The construction and use of an alignment (nomographic) chart for the reduction of volumes of gases, measured over water or potassium hydroxide solution, to standard temperature and pressure are described. J. R. P.

Exact Gas Analytical Methods. E. Ott (*J. Gasbeleucht.*, 1920, **63**, 198—205, 213—220, 246—253, 267—271; from *Chem. Zentr.*, 1920, iv, 397. Compare this vol., ii, 52).—The combustion of carbon monoxide, hydrogen, and methane, separately and when mixed in the presence of platinum, has been examined. The calculation is based on observations of the contraction, carbon dioxide produced, and oxygen consumed. The estimation of a mixture of the three gases by absorption of carbon monoxide by means of cuprous chloride, followed by fractional combustion of hydrogen and methane, has been performed as a control. In addition, the mixed gases are investigated by the fractional combustion of hydrogen and methane on the one hand and of methane on the other in the presence of platinum. The results are fully described, and are designed as standards for a subsequent investigation of the fractional combustion of the gases over copper oxide. A simple apparatus is described which permits the complete analysis of coal-gas, etc., and in which the parts containing the gas remain closed; the estimation of heavy hydrocarbons necessitates the attachment of a connexion for the introduction of liquid, and this can be conveniently arranged. H. W.

The Examination of Naturally Occurring Gases. F. Henrich (*Ber.*, 1920, **53**, [*B*], 1940—1949).—Methods for collecting and analysing natural gases are described. A special apparatus was designed for removing nitrogen for the estimation of the rare gases after removing carbon dioxide and oxygen by the usual methods. The gas is circulated through a hard glass tube, heated at 500°, containing a mixture of calcium and sodium in the ratio 10:1, until there is no further diminution in the volume of the gas. Since the hard glass tube is attacked by the metal and will not stand a vacuum at the temperature employed, it is enclosed in a quartz tube, contact between the two being prevented by means of iron foil or wire. The nitrogen can by this

means be removed completely from about 300 c.c. of gas in from ten to fifteen minutes. The gas from a cold spring near Leupoldsdorf, Bavaria, was found to contain 13·0% of oxygen, 86% of nitrogen, and 1% of rare gas, chiefly argon. Its radioactivity was $0·2398.10^{-6}$ Curie, and it was probably of atmospheric origin.

E. H. R.

The Estimation of Chlorides in Blood. VICTOR C. MYERS and JAMES J. SHORT (*J. Biol. Chem.*, 1920, **44**, 47—53).—A number of methods for the removal of the proteins of the blood were tried but none proved as satisfactory as the use of picric acid recommended by Van Slyke and Donleavy (A., 1919, ii, 239). Accordingly, this method is employed, and the estimation is carried out on the same filtrate as is used for the estimation of creatinine and dextrose. The usual Volhard reagents are used in a diluted form and the precipitate of silver chloride is removed by centrifugalisation.

J. C. D.

The Estimation of Traces of Bromine in Organic Matter. A. DAMIENS (*Compt. rend.*, 1920, **171**, 799—802).—The organs or organic matter are dried at 100—105°, and the dried material mixed with 5 parts of potassium nitrate and 10 parts of sodium carbonate and heated in a silver crucible to just short of fusion. The mass is extracted with water and the solution filtered. In a portion of the filtrate the iodine, as iodide, may be estimated by Labat's method, or by precipitation as silver iodide, liberation as free iodine by means of chlorine, and colorimetric estimation.

In another portion of the filtrate the whole of the halogens are precipitated as their silver salts, which are afterwards decomposed by zinc and sulphuric acid and the bromine estimated, after filtering off the silver, by the method of Denigès and Chelle (A., 1913, ii, 1208). In the presence of iodide, the iodine is removed from the last filtrate by Labat's method, and then the bromine is estimated as above. Chlorine is estimated by difference from the total halogen content.

W. G.

Improvement in the Haldane General Air Analysis Apparatus. ROBERT C. FREDERICK (*Analyst*, 1920, **45**, 409—410).—By making the wide part of the combustion chamber of the apparatus 9 mm. shorter, the stem 25 mm. longer, and placing the mark on the stem 12 mm. from the shoulder, any obscuration resulting from the combustion remains well below the graduation and frequent cleaning is not required. Owing to the longer stem the operation of removing globules of mercury from the inlet tap of the apparatus is also facilitated.

W. P. S.

Simplification of the Kjeldahl Process, particularly for the Estimation of Residual Nitrogen. ARNOLD HAI (*Deutsch. med. Woch.*, 1920, **46**, 428—429; from *Chem. Zentr.*, 1920, iv, 399—400).—The serum (1 c.c.) is treated with water (7 c.c.) and phosphotungstic acid (2 c.c.) and centrifuged for sever

minutes. Five c.c. of the supernatant liquid are filtered and treated with potassium sulphate, a little copper sulphate, and concentrated sulphuric acid (1 c.c.). The action is complete in about five minutes. (A device for the removal of sulphur trioxide fumes is described and sketched in the original.) The contents of the flask are cooled to about 60° and diluted with water (10 c.c.); after complete cooling, 25 c.c. of alcohol are added. Sodium hydroxide solution (33%, 5 c.c.) is introduced and the ammonia is distilled through an uncooled tube, the end of which is considerably constricted, into sulphuric acid (*N*/100, 10 c.c.); excess of the latter is titrated with *N*/100-alkali hydroxide solution. Three drops of sodium alizarin-sulphonate solution (1%) and 6 drops of methylene-blue solution (0·05 gram in 100 c.c. of water) are used as indicator; the colour change is from brownish-green to violet. H. W.

Estimation of Nitrates in Soils. A. L. WHITING, T. E. RICHMOND, and W. R. SCHOONOVER (*J. Ind. Eng. Chem.*, 1920, **12**, 982—984).—One hundred grams of the soil are shaken for three hours with 300 c.c. of 0·5% hydrochloric acid and allowed to settle for eighteen hours; 200 c.c. of the clear supernatant liquid are then transferred to a flask containing 5 grams of sodium peroxide, and boiled until the volume is reduced to 25 c.c. If urea is present, the evaporation is carried to complete dryness. Two hundred c.c. of water are then added, together with 0·5 gram of Devada's alloy, and the mixture is distilled for forty minutes, the distillate containing the ammonia being collected, as usual, in a definite quantity of standardised acid. W. P. S.

Detection of Nitrites. L. THEVENON (*J. Pharm. Chim.*, 1920, [vii], **22**, 336—337).—A red coloration develops at once when a nitrite solution is treated with a few drops of 33% acetic acid and 2 c.c. of 0·5% *p*-aminophenol hydrochloride solution. The reaction, which may be used for the detection of nitrites in drinking water, is not given by nitrates, and the salts occurring in natural waters do not interfere with the test. W. P. S.

Rapid Colorimetric Methods for the Estimation of Phosphorus in Urine and Blood. RICHARD D. BELL and EDWARD A. DOISY (*J. Biol. Chem.*, 1920, **44**, 55—67).—The authors take advantage of the fact that certain reducing agents will reduce phosphomolybdic acid in the presence of molybdic acid without affecting the latter. Quinol was selected as the most suitable reducing agent.

If quinol is added to a faintly acid solution of molybdic acid the mixture will be perfectly colourless when treated with a solution of sodium carbonate and sodium sulphite. When phosphates are present, however, a blue colour is produced which can be compared in the usual manner with a standard.

This forms the basis of methods for the estimation of phosphorus and phosphates in urine and blood. It is stated that the results are

not as accurate as those yielded by a suitable gravimetric method, but that the process is a more convenient one for certain purposes.

J. C. D.

An Extremely Sensitive Colour Test for Phosphates and Arsenates. G. Denigès (*Compt. rend.*, 1920, **171**, 802—804).—The reagent used is a mixture of equal volumes of concentrated sulphuric acid and a 10% solution of ammonium molybdate. To 5 c.c. of the liquid containing phosphate or arsenate, 3—10 drops of the reagent, according to the amount of phosphate present, are added. The mixture is shaken, and one or two drops of a freshly prepared solution of stannous chloride are added. A blue colour is obtained in the presence of a phosphate or an arsenate. Fluorides tend to inhibit the reaction, but this can be overcome by the preliminary addition of boric acid if they are present. W. G.

Estimation of Arsenic and Phosphoric Acids in the Presence of Large Amounts of Salts. Leon Desbourdeaux (*Bull. Sci. Pharmacol.*, 1920, **27**, 225—240, 300—313, 363—372).—By the addition of sodium salts to magnesia mixture, magnesium hydroxide is precipitated in amount depending on the quantity of ammonium salt present.

When arsenic is precipitated as magnesium ammonium arsenate, the precipitation is incomplete after thirty-six hours in the presence of ammonium nitrate, ammonium chloride, or ammonium sulphate; in the first two cases complete precipitation is effected in twelve hours by the addition of magnesium nitrate or chloride in amount equivalent to 1/35th of the ammonium nitrate or chloride present. Complete precipitation is inhibited by sodium sulphate, chloride, or nitrate, even in the presence of the corresponding magnesium salt. Precipitation is complete in thirty-six hours in the presence of potassium nitrate, but in the case of potassium chloride magnesium chloride equivalent to 1/35th of the potassium chloride must be added.

Provided an excess of magnesia mixture is used, the precipitation of phosphoric acid as magnesium ammonium phosphate is complete in hot or cold solution in the presence of ammonium nitrate; precipitation is complete in the cold in the presence of ammonium chloride, but not in the hot, whilst in the presence of ammonium sulphate precipitation is incomplete in all cases. Precipitation is incomplete in the presence of sodium nitrate, chloride, or sulphate with the potassium salts precipitation is satisfactory in warm solutions and is complete in the cold in the cases of the chloride and sulphate.

In estimating phosphoric or arsenic acid as the silver salt in the presence of ammonium, alkali or alkaline earthy nitrate, sulphate or chloride, the solution is acidified, if necessary, with 5—10 c.c. of concentrated nitric acid, silver nitrate is added in amount corresponding with the chloride and phosphate or arsenate present, and then an excess equivalent to 5% of the ammonium salt or 2% of the

potassium salt present; the mixture is rendered barely perceptibly acid by the addition of ammonia, and after half-an-hour the precipitate is collected, washed with 0·2% silver nitrate, and digested on a boiling water-bath for one hour with 1 vol. of a solution of 40 c.c. of concentrated nitric acid and 4 grams of barium nitrate made up to 1 litre. The solution obtained by filtration is free from chloride and sulphate. The residue in the filter is washed with 2 vols. of a solution of 20 c.c. of concentrated nitric acid, 0·5 gram of barium nitrate, and 4 grams of silver nitrate made up to 1 litre; the combined filtrates are rendered barely acid by ammonia, and the precipitate is collected, washed with 0·2% silver nitrate and with water, dried at 150°, and heated at 400° for two hours before weighing. The method, which is applicable to magnesium ammonium phosphate or arsenate, in general tends to give slightly high results. CHEMICAL ABSTRACTS.

Detection of Graphite and its Distinction from Similar Minerals. O. HACKL (*Verh. geol. Reichsanst. Wien*, 1918, 261–262; from *Chem. Zentr.*, 1920, iv, 399).—Simple methods are indicated for distinguishing between carbonaceous substances and oxides of iron or manganese, metallic manganese, and antimony. The following microchemical method is recommended for the detection of even traces of graphite. The substance is completely freed from carbonates by treatment with boiling dilute hydrochloric acid, after which it is washed and dried. The residue is fused with ten times its weight of potassium nitrate, which converts carbon into carbonates, and the product is extracted with a little water. The presence of carbou is shown by the evolution of carbon dioxide after addition of dilute hydrochloric acid. If only traces of carbon are present, a drop is treated successively with strontium acetate and dilute hydrochloric acid; evolution of gas is then readily observed under the microscope, as is also the eventual re-solution of precipitated strontium carbonate.

H. W.

Relationship of Hydrogen-ion Concentration of Natural Waters to Carbon Dioxide Content. R. E. GREENFIELD and G. C. BAKER (*J. Ind. Eng. Chem.*, 1920, **12**, 989—991).—The hydrogen-ion concentration of natural waters may be calculated approximately from the simple mass-law equation of the primary ionisation of carbouic acid, namely, $(H^\cdot)(HCO_3')/(H_2CO_3+CO_2)=3{\cdot}0\times10^{-7}$ (Landolt and Börnstein), or $(H^\cdot)(CO_3'')/(HCO_3')=6{\cdot}0\times10^{-11}$ (Auerbach and Pick). If hydrogen carbonate and carbon dioxide are expressed in terms of CO_2 per litre, $(H^\cdot)=3{\cdot}5\times10^{-7}CO_2/(HCO_3')+1\times10^{-8}$. W. P. S.

Active Carbonic Acid in Drinking Water. I. M. KOLTHOFF (*Chem. Weekblad*, 1920, **17**, 558).—A reply to criticisms, pointing out that the values given by the author (*ibid.*, 390) are not affected by the presence of normal quantities of alkali or magnesium carbonates. [See *J. Soc. Chem. Ind.*, 1920, December.] S. I. L.

Estimation of Potassium as Perchlorate. III. GREGOI P. BAXTER and FRANK E. RUPERT (*J. Amer. Chem. Soc.*, 192 **42**, 2046—2049. Compare A., 1917, ii, 270; this vol., ii, 388).- The solubility of potassium perchlorate has been determined at (and 20° in methyl alcohol, and in ethyl alcohol denaturated wi 5% of methyl alcohol, both solvents containing known percentag of perchloric acid. The solubility in methyl alcohol was ma times greater than that in the denaturated ethyl alcohol, co sequently the former solvent is unsuitable for washing potassiu perchlorate in quantitative work. The solubility in t denaturated ethyl alcohol is practically the same as that in pu ethyl alcohol. The procedure previously described for the esti ation of potassium (*loc. cit.*) was therefore carried out, usi denaturated ethyl alcohol instead of absolute ethyl alcohol. T results show that ethyl alcohol denaturated with 5% of meth alcohol may safely be substituted for ethyl alcohol in washi potassium perchlorate, and that the temperature at which washing occurs is unimportant if the washing liquid employed af the initial extraction is previously saturated with potassi perchlorate. J. F. S

A Microchemical Reaction for Ammonium Sal C. VAN ZIJP (*Pharm. Weekblad*, 1920, **57**, 1345—1348).—See t vol., i, 918.

A New Microchemical "Two-phase Reaction" Magnesium Ammonium Phosphate. HERMANN KUNZ-KRA (*Ber.*, 1920, **53**, [*B*], 1672—1673).—The following reaction, wh is best observed microscopically, is specially suited to the detect of magnesium ammonium phosphate in urinary sediments, may be applied to the detection of phosphates generally. ' solution of the sediment in acetic acid is neutralised with ammo On addition of a drop of silver nitrate solution, an egg-yel cheese-like precipitate of silver phosphate is formed, which appears on addition of a drop of ammonia. At the same time, magnesium ammonium phosphate is precipitated as colour shining prisms united in the form of rosettes. The reaction be applied to the detection of phosphates as cellular enclosure plant tissues. E. H. I

Microchemical Distinction between Sericite and T O. HACKL (*Verh. geol. Reichsanst. Wien*, 1918, 241—242; f *Chem. Zentr.*, 1920, iv, 399).—Since sericite (potassium alumir silicate) frequently contains magnesium and talc (magne silicate) often contains aluminium, the qualitative macrocher tests for aluminium and magnesium give but little informa Complete solution of the mineral is unnecessary for microche investigation; it suffices if the finely powdered mineral is extra with boiling concentrated hydrochloric acid and the solutic evaporated; the residue is dissolved in a little acidified water, one portion is examined for potassium by means of pla

chloride, whilst another part is tested for aluminium with sodium sulphate and cæsium chloride. H. W.

Estimation of Copper (especially in the Analysis of Sugars) by means of Potassium Thiocyanate and Potassium Iodide. G. Bruhns (*Zeitsch. anal. Chem.*, 1920, **59**, 337—359).—Investigation of the conditions controlling the reaction between cupric salts and a mixture of potassium thiocyanate and potassium iodide showed that the following procedure is trustworthy. Twenty c.c. of Fehling's solution and 20 c.c. of the sugar solution (containing not more than 0·4% of sugar) are mixed, boiled for two minutes, 50 c.c. of cold water are then added, and the whole cooled rapidly. Five c.c. of potassium thiocyanate–iodide solution (potassium thiocyanate, 0·65 gram; potassium iodide, 0·1 gram in 5 c.c. of water) are added, followed by 10 c.c. of 0·5*N*-sulphuric acid, and the liberated iodine is titrated with thiosulphate solution (34·4 grams per litre). A control titration is made at the same time with the same quantities of reagents, but without heating, and the difference between the quantities of thiosulphate solution used for the two titrations is a measure of the reducing sugar present. Tables are given showing the amounts of sugar corresponding with various volumes of thiosulphate solution. W. P. S.

Colorimetric Analytical Methods. XIII. Estimation of Mercury in Urine. W. Autenrieth and W. Montigny (*Munch. med. Woch.*, 1920, **67**, 928—931; from *Chem. Zentr.*, 1920, iv, 426).—A colorimetric method is described for the estimation of mercury in urine as mercuric sulphide with the aid of the Autenrieth-Königsberger colorimeter; other metals precipitable by hydrogen sulphide must not be present. H. W.

Volumetric Estimation of Mercury, Iron, and Vanadium in the same Solution. G. Hinard (*Ann. Chim. anal.*, 1920, [ii], **2**, 297—299).—To estimate mercury, iron, and vanadium in sulphuric acid solution, an aliquot portion of the latter is treated with hydrogen sulphide, the mercury sulphide separated, oxidised with bromine, the excess of bromine expelled by heating, the solution then rendered alkaline with potassium hydroxide (precipitated mercuric hydroxide does not interfere), a known excess of standardised potassium cyanide solution is added, and the excess then titrated with silver nitrate solution, potassium iodide being added as indicator. The quantity of cyanide used is equivalent to the amount of mercury present:

$$HgO + 4KCN + H_2O = HgK_2(CN)_4 + 2KOH.$$

The filtrate from the mercury sulphide is boiled to expel hydrogen sulphide, oxidised with bromine, and the iron is precipitated as ferric hydroxide by treating the boiling solution with potassium hydroxide; the ferric hydroxide is dissolved in hydrochloric acid, again precipitated as hydroxide (to remove remaining traces of vanadium), then dissolved in sulphuric acid, and estimated iodo-

metrically: $Fe_2O_3 + 2HI = 2FeO + H_2O + I_2$. Iron and vanadium are then determined together iodometrically in a separate portion of the original solution: $V_2O_5 + 2HI = V_2O_4 + H_2O + I_2$. If the original solution also contains mercurous, ferrous, and vanadyl salts, the first may be separated by treatment with sodium chloride solution, whilst the proportions of ferrous and vanadyl salts may be estimated by iodometric titration before and after oxidation.

W. P. S.

Rapid Method for the Analysis of Light Aluminium Casting Alloys. Russell M. Berry (*J. Ind. Eng. Chem.*, 1920, **12**, 998—1000).—The accuracy of the rapid method described depends on the facts that a larger amount of the alloy can be taken, and that most of the aluminium is removed at the outset from all the other metals, except zinc. The alloy is dissolved in 25% sodium hydroxide solution, and the insoluble residue (tin, copper, lead, iron, nickel, magnesium, part of the manganese, and traces of aluminium) washed with dilute sodium hydroxide solution. The filtrate is acidified with formic acid, the zinc precipitated with hydrogen sulphide, the zinc sulphide digested with hot dilute hydrochloric acid, the liquid filtered, and the filtrate and washings titrated with potassium ferrocyanide solution. Tin is estimated by digesting the alkali-insoluble portion with nitric acid, filtering the solution, washing the residue, and extracting it with ammonium polysulphide and ammonium chloride. The filtrate containing the tin is acidified with acetic acid, and the tin precipitated as sulphide, ignited, and weighed as SnO_2. Copper and lead are estimated electrolytically in the first filtrate from the tin, the copper being deposited on the cathode, and the lead on the anode. Iron is precipitated as hydroxide in the electrolyte from the copper and lead estimations, the washed precipitate dissolved in dilute hydrochlori acid, and the iron reduced with stannous chloride and titrated witl standard potassium permanganate solution. The filtrate from th iron (and traces of aluminium) is used for the precipitation of th nickel by means of dimethylglyoxime, whilst magnesium is precipi tated as phosphate in the filtrate from the nickel. Manganese i estimated by treating the alloy with sodium hydroxide solution adding nitric acid in excess, and then a few crystals of silve nitrate, oxidising the solution with ammonium persulphate, an titrating it with standard arsenite solution. For the estimation c silicon the alloy is dissolved in a mixture of nitric and sulphur acids and water, the solution evaporated to dryness, the residu treated with hydrochloric acid and hot water, and the silica ignite weighed, treated with hydrofluoric acid, and again weighed. [Se further, *J. Soc. Chem. Ind.*, 1920, December.]

C. A. M.

Detection of Manganese in the Presence of Phosphate D. H. Wester (*Ber. Deut. pharm. Ges.*, 1920, **30**, 381—382. Com pare this vol., ii, 334, 389).—A further criticism of the meth described by Schmidt (*loc. cit.*).

W. P. S.

Detection of Manganese in the Presence of Phosphates. ERNST SCHMIDT (*Ber. Deut. Pharm. Ges.*, 1920, **30**, 383).—A reply to Wester (compare preceding abstract). The manganese should be first separated by precipitation as sulphide in order to remove phosphates. W. P. S.

Separation of Iron from Aluminium by Precipitation as Prussian Blue. HARRISON HALE and G. O. BURR (*J. Amer. Chem. Soc.*, 1920, **42**, 2056—2058).—The quantitative separation of iron from aluminium as Prussian blue cannot be effected, since the aluminium reacts with the excess of potassium ferrocyanide, forming a jelly which cannot be handled. The precipitate of Prussian blue cannot be successfully filtered, even after apparently perfect coagulation. J. F. S.

Analysis of Molybdenum, Cobalt, and Chromium Alloys. J. R. CAMP and J. W. MARDEN (*J. Ind. Eng. Chem.*, 1920, **12**, 998).—The alloy is dissolved in aqua regia, the excess of which is expelled by heating the solution with 3 c.c. of sulphuric acid. The liquid is cooled, diluted to 100 c.c., saturated with hydrogen sulphide, and heated in a closed bottle for an hour in boiling water. The precipitate of molybdenum sulphide is separated, washed, dissolved, reprecipitated, finally ignited for two hours in a muffle, and the residue weighed as MoO_3. The cobalt is precipitated from the boiling filtrate with sodium peroxide, the precipitate washed with dilute hydrogen peroxide, and the black cobaltic hydroxide ignited and weighed at Co_3O_4. In most cases reprecipitation of the cobalt is necessary to ensure complete separation. The filtrate is acidified and the chromates titrated with ferrous ammonium sulphate solution, potassium ferricyanide being used as an external indicator. [See also *J. Soc. Chem. Ind.*, 1920, December.] C. A. M.

Identification of Tin in Ores. AUGUST ZÖLLER (*Chem. Zeit.*, 1920, **44**, 797—798).—A portion of the mineral or ore is placed on a piece of zinc foil and moistened with a drop of hydrochloric acid; if tin is present a grey film of metallic tin appears on the surface of the mass within a few minutes. W. P. S.

Estimation of Gold. PAUL DRAWE (*Zeitsch. angew. Chem.*, 1920, **33**, 272).—The following method is recommended for the estimation of gold in alloys also containing silver and copper. From 0·4 to 0·5 gram of the sample is dissolved in aqua regia, the solution evaporated to dryness, and the residue treated with hydrochloric acid and water. After the silver chloride has been separated by filtration, the solution is rendered alkaline with potassium hydroxide, boiled, and the cupric oxide collected on a filter. The filtrate is acidified with hydrochloric acid, then rendered slightly alkaline with potassium hydroxide, hydrogen peroxide is added, the mixture boiled, and the metallic gold collected, ignited, and weighed. W. P. S.

Quantitative Organic Microanalysis. R. CORNUBERT (*Rev. gén. sci.*, 1920, **31**, 442—455).—The paper describes the origin and development of the micro-balance and its manipulation. Detailed descriptions are given for the micro-estimation of carbon, hydrogen, nitrogen, halogens, sulphur, sodium, potassium, calcium, barium, silver, gold, terbium, platinum, chromium, copper, phosphorus, methoxyl, carboxyl, and the :N·OMe group, and for the micro-determination of molecular weights, the methods being essentially those of Pregl and Dubsky. CHEMICAL ABSTRACTS.

Use of Reduced Copper in the Elementary Analysis of Organic Compounds. EMILE CHERBULIEZ (*Helv. Chim. Acta*, 1920, **3**, 652—653).—At a red heat, copper containing small proportions of iron or zinc causes appreciable reduction of carbon dioxide to carbon monoxide, and is, therefore, unsuitable for use in the determination of carbon and hydrogen in nitrogen compounds by combustion or in the estimation of nitrogen (compare Perrot, *Compt. rend.*, 1859, **48**, 53). T. H. P.

Absorbent Solution for Heavy Hydrocarbons. ALEX. PIECHOTA (*Chem. Zeit.*, 1920, **44**, 797).—A saturated solution of potassium dichromate in concentrated sulphuric acid is an efficient absorbent for heavy hydrocarbons in gas analysis. W. P. S.

Analysis of Aromatic Nitro-compounds by means of Titanium Chloride. F. L. ENGLISH (*J. Ind. Eng. Chem.*, 1920, **12**, 994—997).—Mononitro-hydrocarbons are exceedingly resistant to reduction by titanium chloride, but the presence of positive or negative substituents, with the exception of chlorine, in the nucleus facilitates the reduction of the nitro-group. Further, it would appear that the orientation of the substituents with respect to the nitro-group has no appreciable effect; thus, *m*- and *p*-nitroaniline are reduced readily, as are *o*- and *p*-nitrophenols, *o*- and *m*-nitro-*p*-toluidines, and two of the nitrosalicylic acid isomerides. Conversely, *o*- and *p*-chloronitrobenzene are about equally refractory. W. P. S.

Detection of Methyl Alcohol as Methyl *p*-Bromobenzoate. W. AUTENRIETH (*Arch. Pharm.*, 1920, **258**, 1—14).—Methyl alcohol in warm dilute aqueous solution is converted by *p*-bromobenzoyl chloride in presence of 10% sodium hydroxide into the well-characterised and easily crystallisable methyl *p*-bromobenzoate. The test is sufficiently sensitive to detect 0·05 gram of methyl alcohol, even in extreme dilution. The ester is recognisable by its anise-like odour, its m. p., 77—78°, its bromine content by the Carius method, and its conversion by aqueous ammonia into *p*-bromobenzamide, m. p. 188°. The crystalline ester can readily be isolated, even in presence of a large excess of the ethyl ester, which is liquid at temperatures as low as −16°. Thus, from a solution containing 0·2% of methyl and 0·8% of ethyl alcohol,

crystals of the methyl ester were obtained, the method being to extract with ether and crystallise from aqueous alcohol the residue from the ethereal extract. Similarly, 5% of methyl alcohol in a spirit of wine was detected after one fractional distillation. Minute quantities of methyl alcohol in urine can likewise be detected after distilling with phosphoric acid to retain ammonia, and redistilling the distillate with alkali hydroxide to remove phenols. Although the method does not lend itself to an exact estimation of methyl alcohol, yet, when it is a question of the estimation of small quantities in dilute aqueous solution, approximate figures may be obtained, as, according to the results of a series of experiments, fairly constant amounts of 55—65% of the theoretical quantity of methyl *p*-bromobenzoate were isolated. G. F. M.

Titrations with Surface-active Substances as Indicators. IV. The Buffer System in Physiological Solutions (Wort and Beer) as Determined by the Application of Surface-active Substances as Indicators. WILHELM WINDISCH and WALTHER DIETRICH (*Biochem. Zeitsch.*, 1920, **106**, 92—109).—Wort and beer, as well as their ultra-filtrates, show very little capillary activity on addition of $N/10$-sodium hydroxide and $N/10$-hydrochloric acid, which suggests that they contain small quantities of capillary-active fatty acids. Wort and beer are amphoteric, as they manifest a lowering in the surface tension on the addition of sodium undecoate (acid indicator) and eucupine dichloride (basic indicator). The titrations indicate the following buffer system in wort: free organic acids–secondary phosphate ⇌ primary phosphate–organic salts. On fermenting, the excess of carbon dioxide changes the equilibrium, as follows: free organic acids–bicarbonate ⇌ primary phosphate–organic salt (compare this vol., ii, 48, 706, 707). S. S. Z.

The Colorimetric Estimation of Phenol in Urine. M. WEISS (*Biochem. Zeitsch.*, 1920, **110**, 258—265).—The method described by the author for the estimation of tyrosine with Millon's reagent (this vol., ii, 135) can also be employed for the estimation of hydroxyphenyl derivatives in urine. The latter have, however, to be previously liberated from the acids with which they are combined by means of hydrolysis. In disease, there is an increase in the excretion of phenol. S. S. Z.

Estimation of Very Small Quantities of Dextrose. PERRIER (*J. Pharm. Chim.*, 1920, [vii], **22**, 337—344).—A method, proposed originally by Bougault (A., 1917, ii, 395), and depending on the oxidation of aldoses by iodine in alkaline solution, is applicable to the estimation of very small quantities of dextrose. Two hundred c.c. of the sugar solution (containing about 0·17 gram per litre) are mixed with 200 c.c. of $N/200$-iodine solution and about 7 c.c. of 1·5% sodium carbonate solution, and the mixture is diluted to 1000 c.c.; after two hours, the mixture is acidified with hydrochloric acid and titrated with $N/100$-thiosulphate solution.

0·2 C.c. is deducted from the volume of iodine solution require to oxidise the sugar. The method may be used for the estimatio of dextrose in body fluids. W. P. S.

Preservation of Specimens of Blood intended for Blood sugar Estimations. W. Denis and Martha Aldrich (*J. Bio Chem.*, 1920, **44**, 203—206).—One drop of commercial form aldehyde to 5 c.c. of oxalated blood appears to be a satisfactor preservative. It does not interfere with the subsequent estim ation. J. C. D.

Folin and Wu's Methods for the Estimation of th Sugar and the Nitrogenous Constituents of the Blood R. Delaby (*Bull. sci. pharmacol.*, 1920, **27**, 372—374).—A revie of the latest method of Folin and Wu for the estimation of suga in the blood, and the statement that these authors advocate i correspondence the use of a urease paper for the estimation of urea This paper is made by dipping filter paper into the filtrate fro a mixture of 30 grams of jack-bean powder, 15 grams of pe mutite, and 200 c.c. of 16% ethyl alcohol. Two to three sq. cm of the paper are used for each estimation.

Chemical Abstracts.

Estimation of Small Amounts of Reducing Sugar in th Body Fluids. L. de Saint-Rat and J. Ronfaut (*Bull. sc. pharmacol.*, 1920, **27**, 289—293).—To 5 c.c. of solution contai ing from 0 to 8 mg. of reducing sugar are added 5 c.c. each o Bertrand's copper and alkali solutions, and the mixture is place in a boiling-water bath for twenty minutes. To prevent evapo ation, a glass bulb is placed in the mouth of the tube. Identic conditions of dilution must be scrupulously observed. The blan obtained with water and the 10 c.c. of alkaline copper solutio under these conditions is equivalent to 0·78 mg. of copper. Th copper oxide formed is filtered on asbestos by gentle suction i such a way as to prevent undue contact with air. This is accom plished by closing the filtering tube with a perforated stoppe through which passes a glass tube to the reaction test-tube, th contents of which are slowly aspirated over into the filtration tu by the same suction stream that brings about filtration. The pr cipitate is dissolved by intermittently aspirating two 5 c.c. lots ferric solution (which has been proved to have no reducing acti on permanganate solution) through the tube. The reaction tes tube is washed twice with 5 c.c. of the ferric solution, and th tube and filter are washed with water. The filtrate is titrated wi 0·2*N*-permanganate prepared according to Halversen and Ber heim's method. A table and chart are given of the mg. dextrose per mg. of copper obtained. Body fluids, such as cerebr spinal fluids, are deproteinised by first heating the solution on th water-bath with equal amounts of zinc and lead acetates, measured on the tip of a knife blade, and filtering.

Chemical Abstracts.

Identification of Acids by Phenacyl Bromide. H. E. Cox (*Analyst*, 1920, **45**, 412).—When using phenacyl bromide (ω-bromoacetophenone) for the esterification and identification of acids (compare Rather and Reid, A., 1919, i, 157), care should be taken that the substance does not come into contact with the skin, since even small quantities produce very painful blisters.

W. P. S.

Comparison of Methods for Estimating the Iodine Number of Fats. W. Devrient (*Ber. Deut. pharm. Ges.*, 1920, **30**, 361—366).—Estimations of the iodine number of elaidic acid by different methods yielded the following results: Hübl method, 80·3; Waller method, 80·0; Winkler method, 80·8; Wijs method, 80·8; Hanuš method, 82·5. The author prefers the last method, as being the most simple and rapid, and because the result obtained is nearer the theoretical value, 90, than are those given by the other methods. W. P. S.

Microchemical Detection of Cyanic Acid. R. Fosse (*Compt. rend.*, 1920, **171**, 722—723).—Silver cyanate crystallises from hot aqueous solution in a definite microcrystalline form, by means of which it can be identified. When silver cyanate, potassium chloride, and cobalt acetate are ground together in the solid state, a deep blue colour is obtained, which disappears on the addition of water and reappears on the addition of alcohol. The blue colour is due to the formation of potassium cobalticyanate, which may be distinguished from the cobaltithiocyanate in that only the latter gives a colour with amyl alcohol. Dilute acids do not destroy or decolorise the cobalticyanate. Ferric chloride gives a red colour with the cobaltithiocyanates, but not with the cobalticyanates. Finally, if silver cyanate is ground with hydroxylamine hydrochloride, and a drop of ferric chloride solution added to the product, a violet-blue coloration is produced.

W. G.

Estimation of Urea in Blood by Xanthhydrol. W. Mestrezat and (Mlle) Marthe Paul Janet (*J. Pharm. Chim.*, 1920, [vii], **22**, 369—377).—See this vol., ii, 645.

Identification of Sulphonal and Trional. Walther Zimmermann (*Apoth. Zeit.*, 1920, **35**, 27).—Sulphonal has m. p. 125—126°, and trional has m. p. 76°. When 0·1 gram of sulphonal or trional is heated in a test-tube with 0·1 gram of sodium salicylate, an odour of mercaptan is observed; if the mixture is treated with five drops of alcohol and five drops of concentrated sulphuric acid, and, after five minutes, heated with the addition of a further five drops of sulphuric acid, a turbid, red solution is obtained, which has an odour of methyl salicylate. A violet-coloured residue is obtained when a mixture of 0·2 gram of sulphonal or trional and 0·02 gram of sodium salicylate is ignited in a porcelain basin; this residue gives a violet solution

when treated with a drop of water. The addition of a drop of dilute hydrochloric acid changes the colour to yellow, a brown flocculent precipitate separates, and sulphur dioxide is evolved. Acetanilide, antipyrin, and phenacetin yield black residues when heated with sodium salicylate, veronal a green residue, and santonin a red residue. W. P. S.

Behaviour of Silico- and Phospho-tungstic Acids towards Alkaloids. A. Heiduschka and L. Wolff (*Schweiz. Apoth. Zeit.* 1920, **58**, 213—218, 229—233).—For gravimetric estimations with silicotungstic acid, a 0·01*N*-solution of the acid (of pre-determined water content) is prepared and standardised by means of a 0·01*N* solution of a quinine salt in the presence of 1% hydrochloric acid; the precipitate is collected and incinerated, and the factor is calculated from the weight of the residual $SiO_2,12WO_3$.

The compounds were examined as follows. A 0·01*N*-solution of the alkaloid is prepared equivalent to 4 mols. : 1 mol. of silicotungstic acid. Corresponding volumes of the alkaloid and silicotungstic acid solutions are mixed, 1% hydrochloric acid is added and the precipitate is collected after one hour. With quinine, cinchonine, papaverine, and narcotine, precipitation occurs readily; coniine in small quantities is not precipitated. Quinine, cinchonine, sparteine, and nicotine form compounds of the type $SiO_2,12WO_3,2H_2O,2B,xH_2O$ (or Si : B = 1 : 2). Caffeine with 1% hydrochloric acid is barely precipitated, but with 3% hydrochloric acid a 1 : 3-compound is obtained. Morphine, codeine, thebaine, atropine, and cocaine yield 1 : 4-compounds. Morphine in the presence of 1—3% sodium chloride yields a 1 : 2-compound; with strychnine, brucine, narcotine, papaverine, colchicine, aconitine and veratrine, more silicotungstic acid is contained in the precipitate with greater concentrations of the electrolyte, but at lower concentrations the equilibrium is displaced towards the ratio 1 : 4. When precipitated from dilute alcoholic solution (in the absence of hydrochloric acid), strychnine, brucine, veratrine, and aconitine yield exactly 1 : 4-compounds.

In volumetric analysis, a moderate excess of the silicotungstic acid solution is added, then 1% sodium chloride, and, after filtering, the solution is titrated with sodium hydroxide with methyl-red as indicator; the method is inapplicable in the presence of albumin.

For the gravimetric estimation of alkaloids with phosphotungstic acid, the latter is used in 0·01*N*-solution, the factor being determined as above from the weight of $HPO_3,12WO_3$ obtained after incineration. With quinine, cinchonine, sparteine, and nicotine the ratio P : alkaloid = 2 : 3, the formula of the compound being $2[P(W_2O_7)_6]H_7,3B$; this composition is constant when the precipitation is effected in the presence of less than 1% of hydrochloric acid. With all other alkaloids, the ratio is 1 : 3 at low concentrations of hydrochloric acid. This method is preferable to the silicotungstic acid method for aconitine and nicotine.

Small amounts of alkaloids can be estimated by means of the opalescence produced with silico- or phospho-tungstic acid.
CHEMICAL ABSTRACTS.

The Conductometric Titration of Alkaloids and their Salts. I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, **112**, 196—208).—Alkaloids or their salts can be titrated with satisfactory accuracy by the conductometric method in very dilute solutions. The alkaloids themselves are titrated with acid; the conductivity rises steadily from the commencement of the titration, and at the point where salt formation is complete, the rate of increase of conductivity suddenly augments. The alkaloid salts are titrated with alkali, and in these cases, also, the conductivity curve rises throughout the titration, with a sharp break at the neutral point. In the case of a basic salt, such as quinine hydrochloride, in which the second dissociation constant is not too small, the acid content can be determined by titration with alkali and the alkaloid by means of acid. Titrations of alkaloids or their salts with indicators, such as phenol- or thymol-phthalein for alkali and methyl-red or dimethyl-yellow for acid titration, generally give uncertain results, because a solvent, such as alcohol or chloroform, has to be used. For the conductometric titration of the alkaloid salts, no solvent need be used, but for the titration of the free alkaloids they are generally dissolved in 55% alcohol. The alkaloid salts examined included quinine hydrochloride, strychnine nitrate, cocaine and tropacocaine hydrochlorides, novocaine, atropine sulphate and morphine and ethylmorphine hydrochlorides. In the case of morphine hydrochloride, it was found best to titrate in 50% alcohol; no distinct break was found in the conductivity curve at the neutral point, but, on continuing the titration with alkali, morphinate formation was indicated by a very sharp break in the curve. The alkaloid bases examined included quinine, hydrastine, codeine, morphine, nicotine, theobromine, and caffeine. The last is a very weak acid with a dissociation constant less than 10^{-14}, whilst that of theobromine is about 10^{-10}. Accordingly, it was found that theobromine could be exactly estimated in a mixture with caffeine by dissolving in alkali and titrating back with acid. The break in the conductivity curve was quite distinct.
E. H. R.

Estimation of Cystine. Y. OKUDA (*J. Coll. Agr. Imp. Univ. Tokyo*, 1919, **7**, 69—76).—The cystine should be present in a solution with a volume of 10 c.c. and containing from 5 to 10% of hydrochloric or sulphuric acid. To this solution are added 10 c.c. of 20% sodium bromide solution. The cystine is now titrated with 0·05*N*-sodium bromate, taking as the end-point a faint yellow colour, which remains for one minute; 1 c.c. of the bromate solution equals 0·00721 gram of cystine. The cystine is oxidised to cysteic acid by bromine, which is formed by the reaction between

the bromide and bromate in the acid solution; 1 mol. of cystine requires 10 atoms of bromine in this oxidation. Of the amino-acids, other than cystine, which are precipitated by phosphotungstic acid, only histidine absorbs bromine; however, the velocity of the reaction between cystine and bromine is so much greater than that of the reaction between histidine and bromine that the presence of histidine does not influence the titration of cystine, provided the titration be stopped when the solution becomes faintly yellow, and the colour remains constant for one minute. Even as small an amount of cystine as a few mg. may be accurately estimated by this method; the result is not influenced by the concentration of either the cystine or the acid. If a solution contains both cystine and tyrosine, the latter will react with 2 atoms of bromine. The titration is made as usual; the cystine is oxidised and estimated as barium sulphate, and the tyrosine is calculated, or the tyrosine is estimated colorimetrically, and the cystine is calculated. This procedure may be applied in analysis of the cleavage products of proteins. CHEMICAL ABSTRACTS.

Estimation of Morphine in Opium. AXEL JERMSTAD (*Ber. Deut. pharm. Ges.*, 1920, **30**, 398—402).—The following modification of the Helfenberger method is recommended: 6 grams of the powdered opium are ground with 6 grams of water, the mixture is rinsed into a flask, and water is added to make the total weight 54 grams. After thirty minutes, the mixture is filtered, 40 grams of the filtrate are treated with 2 grams of ammonia solution (17 grams of ammonia and 83 grams of water), filtered, and 36 grams of this filtrate are shaken for ten minutes in a flask with 7 grams of ether and 4 grams of ammonia; 10 c.c. of ether are then added, and, after thirty minutes, the ethereal solution is poured through a small filter. The crystals in the flask are washed with 10 c.c. of ether, then with three successive quantities of 5 c.c. of water saturated with ether, and dried at 100°. The crystals are then dissolved in 25 c.c. of $N/10$-hydrochloric acid, 75 c.c. of water are added, and the excess of acid is titrated with $N/10$ sodium hydroxide solution, using methyl-red as indicator. One c.c. of $N/10$-acid is equivalent to 0·0285 gram of anhydrous morphine. W. P. S.

New Method for the Estimation of the Total Minor Alkaloids, of Narcotine, and of Papaverine in Opium Preparations of the Type of Pantopon. E. ANNELER (*Arch. Pharm.*, 1920, **258**, 130—137. Compare A., 1912, ii, 818).—The following process for the estimation of the total minor alkaloids (with the exception of narceine) is recommended. The mixture of hydrochlorides (1·5 grams) is dissolved by warming in water (8 c.c.), and pure benzene (90 grams) is added. Powdered sodium carbonate (0·5 gram) is gradually added with shaking, and the mixture is allowed to remain for half an hour, with frequ

vigorous agitation. Water is absorbed by the addition of anhydrous sodium sulphate (5 grams), followed by agitation during five minutes, and further addition of tragacanth powder (0·5 gram). After thirty minutes, the benzene solution is rapidly filtered, and 80 grams of it (or other aliquot portion) are evaporated to dryness in a tared flask on the steam-bath. The residue is dissolved in a few c.c. of warm alcohol, the solvent is removed, and the residue weighed after being dried for half an hour in the steam-oven. The results agree with those obtained by the method of Mannich and Schwede, to which the empirical correction of 1·5% has been made.

Narcotine and papaverine are estimated in the minor alkaloids in the following manner. The minor alkaloids (obtained in the process outlined above) are dissolved in benzene (6 c.c.), the solution is treated with 1 c.c. of alcoholic potassium hydroxide solution (1 c.c.=0·14—0·16 gram KOH), and the mixture is allowed to remain at the ordinary temperature, with frequent shaking, during half an hour. It is then poured into a separating funnel (100 c.c.) the flask is rinsed with three portions of benzene (each 10 c.c.) and subsequently three times with aqueous sodium hydroxide solution (2%; 7 c.c. each time), and the solution is well shaken in the separator. The aqueous solution is run into a second separating funnel, and the benzene solution is twice washed with sodium hydroxide solution (10 c.c. each time). The combined aqueous extracts are shaken with three portions of chloroform (5 c.c.) and run into a beaker, where, after being neutralised with hydrochloric acid, they are diluted to 100 c.c. Concentrated hydrochloric acid (36%; 3 c.c.) is added, and the solution is heated for twenty minutes at 80—90°, immediately cooled, and poured into a separating funnel; after addition of an excess of sodium carbonate solution, the narcotine is extracted with benzene (20+10+10+5 c.c.) or chloroform. The extract is dried with a little tragacanth powder and filtered into a weighed flask, and evaporated to dryness on the water-bath; the residue is again dissolved in a little warm alcohol, the solvent is removed, and the residue dried and weighed.

The benzene solution remaining in the separating funnel (see above) is filtered into a flask and evaporated to dryness, the chloroform extract being similarly treated in the same flask. The residue is dissolved in a mixture of water (10 c.c.) and hydrochloric acid (10%; 1 c.c.), the solution is filtered into a small beaker, and the filter paper thrice washed with water (5 c.c.). Ammonia solution (2%) is cautiously added until a faint, permanent turbidity results, followed by solid sodium acetate (2 grams). The mixture is allowed to remain for twenty-four hours, with frequent stirring and rubbing of the walls of the beaker, whereby the papaverine is precipitated as a glassy or powdery mass. The mother liquor is passed through a small filter, which is subsequently washed three times with water (5 c.c.). The paper is returned to the beaker

and, after both have been dried, the papaverine is dissolved in warm alcohol. The solution is filtered into a weighed flask, the solvent is removed, and the residue is weighed after being dried during an hour at 98°.

The method is applied to opium powder in the following manner. The powder (6·66 grams) is frequently shaken in a corked flask during three hours with a mixture of water (115 c.c.) and hydrochloric acid (10%; 5 c.c.), and the paste is then filtered by means of a suction pump. 102 C.c. of the filtrate (=5·55 grams of opium powder) are rendered alkaline by the addition of sodium carbonate solution (10%; 23 c.c.), and extracted with chloroform (20+10+10+10 c.c.). The extract is dried with a little tragacanth powder, filtered, and evaporated to dryness after addition of alcohol (5 c.c.). The residue is dissolved in hydrochloric acid (1%; 8—10 c.c.), the solution is agitated with benzene (100 c.c.) and sodium carbonate (1 gram) during fifteen minutes, and the estimation is completed as with pantopon. H. W.

Proteinogenous Amines. VII. Colorimetric Estimation of Histidine in Protein and Protein-containing Matter. MILTON T. HANKE and KARL K. KOESSLER (*J. Biol. Chem.*, 1920, **43**, 527—542).—The method is stated to be simple, rapid, and direct, but may be no more accurate than those described by Kossel and Kutscher and by Van Slyke.

The material is hydrolysed by boiling with hydrochloric acid, and the acid and any volatile phenols removed by vacuum distillation. Ammonia and humin are removed by treatment with lime, and the solution divided into two fractions by means of phosphotungstic acid. The phosphotungstate precipitate is treated with water and sufficient 3*N*-sodium hydroxide to give a clear solution, which is then used for the colorimetric determination by the method previously described (Koessler and Hanke, this vol., ii, 67). The method cannot be used for estimations on protein material that has undergone putrefactive changes, since histamine and tyramine are precipitated by the phosphotungstic acid and give the colour reaction. J. C. D.

The Separation of Histidine from Arginine. H. KOSSEL and S. EDLBACHER (*Zeitsch. Biol. Chem.*, 1920, **110**, 241—245. Compare A., 1907, i, 107).—The presence of arginine is not necessary in order to effect the precipitation of histidine. S. S. Z.

Proteinogenous Amines. VIII. Colorimetric Estimation of Histamine in Protein and Protein-containing Matter. MILTON T. HANKE and KARL K. KOESSLER (*J. Biol. Chem.*, 1920, **43**, 543—556).—A dry solid is hydrolysed directly with 20% hydrochloric acid for thirty hours. When the material contains

water, it must first be treated with alcohol until the concentration of this solvent is 75%. The mixture is then made faintly acid with acetic acid, and the proteins are coagulated by heating on the water-bath for one or two hours. The mixture is cooled and filtered, and the alcohol removed from each fraction by evaporation. The dry material is employed for hydrolysis. After the hydrolysis is completed, the hydrochloric acid is removed by vacuum evaporation at 60°, and the residue is dried at 80° for one hour.

Ammonia is removed by another vacuum distillation after an excess of lime and dilute alcohol have been added, and by filtration of the fluid after the ammonia has been removed, the humin matter is also separated.

The alkaline filtrate is acidified with hydrochloric acid, and basic substances precipitated with phosphotungstic acid. This precipitate, which contains the proteinogenous amines as well as the dibasic amino-acids, is well washed and decomposed with hot saturated solution of barium hydroxide. After removal of the excess of barium from the filtrate by sulphuric acid, the liquid is evaporated to dryness and dissolved in a very small quantity of water, and made up to known volume. The histamine is extracted from an aliquot portion of this liquid by making strongly alkaline with solid sodium hydroxide and extracting with amyl alcohol several times. The combined amyl alcohol extracts are washed several times with normal sulphuric acid, and the acid fractions neutralised with barium hydroxide while warm. The filtrate from the barium sulphate contains all the histamine, but may also contain traces of histidine. A re-extraction with amyl alcohol after making alkaline with sodium hydroxide is necessary to separate these two substances entirely. From the histamine fraction the histamine is precipitated by silver nitrate and baryta, and the resulting silver compound decomposed by means of hydrochloric acid. The final histamine fraction is then estimated colorimetrically, as described in a previous paper (this vol., ii, 67). Quantities as small as 0·1 mg. of histamine can be accurately determined by this method, even in the presence of protein substances. No evidence of the presence of histamine in caseinogen could be detected by this method, but this protein may contain a substance which possesses a similar depressor action when tested by physiological methods.

Histamine was not found present in 75 c.c. of human blood serum. J. C. D.

Use of Ethyl Acetate as a Precipitating Reagent for Proteins. A. Mabie (*Bull. Sci. Pharmacol.*, 1920, **27**, 135—136; from *Chem. Zentr.*, 1920, iv, 315. Compare this vol., ii, 398).—The detection of protein by the turbidity which results when its aqueous solution is covered with a layer of ethyl acetate is more readily effected in this manner than with any other organic solvent which is soluble in water. H. W.

The Influence of Tyrosine and Tryptophan on th Coloration of the Two Phases of the Xanthoprotei Reaction. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 191 **107**, 203—210).—The intensity of the coloration produced t tyrosine and tryptophan in the acid phase (phase *a*) and in tl alkaline phase (phase *b*) in the xanthoproteic reaction w estimated quantitatively against standard solutions of norm potassium chromate and dichromate and a mixture of dichroma and permanganate. The results showed that, in phase *a*, trypt phan reacted three times as intensely as tyrosine; in phase on the other hand, tyrosine yielded a coloration five times as inten as that caused by tryptophan; in other words, tryptophan ac three times as intensely in phase *b* as in phase *a*, whilst the colo ation yielded by tyrosine in phase *b* is forty-five times as stror as that yielded by it in phase *a*. S. S. Z.

Some Biochemical Colour Tests. II. The Adan kiewicz Protein Reaction. The Mechanism of tl Hopkins-Cole Test for Tryptophan. A New Colo Test for Glyoxylic Acid. WILLIAM ROBERT FEARON (*Biochem.* 1920, **14**, 548—563. Compare A., 1918, ii, 462).—On warmi with 1% pyrogallol in sulphuric acid, glyoxylic acid gives a de blue colour, changing to carmine when the liquid is diluted wi water; it is restored when an excess of sulphuric acid is aga added. The blue colour is not given by oxalic acid or by any its simple derivatives, which do not give rise to glyoxylic ac under the conditions of the test. With the aliphatic aldehydes, red colour is given. An intermediate shade of purple is given formaldehyde in the presence of glyoxylic acid, and the test is value in the detection of aldehydes in ether. Syrupy phospho acid may also be used in place of sulphuric. The chemistry the test has not been completely investigated. The coloured co densation products are probably hydroxy-derivatives of xanthe On applying this reagent to solutions of formaldehyde in sulphu acid in the presence of oxidising agents, under conditions of t Rosenheim test (A., 1906, ii, 508), no evidence of the formati of glyoxylic acid was obtained. This supports the view express by Rosenheim that the test depends on formaldehyde. It appe probable, however, that both formaldehyde and glyoxylic acid fo coloured derivatives with tryptophan.

Sulphuric acid is not a good condensing agent for these tes and use was made of glacial acetic acid saturated with hydrog chloride or phosphoric acid. For production of a colour condensation product, however, an oxidising agent, such hydrogen peroxide, is necessary. The separation of the conden tion products was found to be difficult, but was attained by fr tional precipitation with pure ether.

A number of condensation products have been prepared. T leuco-compounds are somewhat unstable, readily being oxidised the coloured complexes.

As precipitated, the pigments are all hydrochlorides of nearly colourless bases. The free pigments are amorphous, deeply coloured powders showing melting points in the region of 300°.

The following compounds are described: *scatole-formaldehyde-red*, $C_{19}H_{16}N_2X$; *scatole-glyoxylic-red*, $C_{20}H_{16}N_2X$; *scatole-benzaldehyde-purple*, $C_{25}H_{20}N_2X$. Similar condensation products of tryptophan with formaldehyde, glyoxylic acid, and benzaldehyde are described. Brief reference is made to condensation products of carbazole and aldehydes. The formation of these pigments constitutes a good test for carbazole. Salicylaldehyde is recommended as a useful qualitative reagent for indole derivatives.

J. C. D.

Detection of Albumin in Urine. WILHELM RADO (*Gyògyaszat*, **6**, 66—67; from *Chem. Zentr.*, 1920, iv, 400).—The test is applied by the addition of sulphuric acid (5%; about 1 c.c.) and sodium nitroprusside solution (eight to ten drops) to the filtered urine (5—10 c.c.); in sensitiveness and clinical applicability, the test is equal to Boedeker's method with potassium ferrocyanide and acetic acid.

H. W.

Estimation of Albumin in Urine by means of Aufrecht's and Esbach's Albuminimeters. BRUNO WIENSS (*Pharm. Zentr.-h.*, 1920, **61**, 535—537).—Comparative estimations showed that the results obtained by the Aufrecht apparatus agreed closely with those found by the gravimetric method, whilst in every case the Esbach results were too high.

W. P. S.

Gravimetric Estimation of Albumin in Urine. G. PÉGURIER (*Ann. Chim. anal.*, 1920, [ii], **2**, 332—335).—The estimation of albumin in urine may be accelerated by combining the method of heating with Méhu's method of precipitation with phenol. For this purpose, a modified reagent, consisting of 10 grams of colourless, crystallised phenol, 10 grams of powdered citric acid, and 20 grams of 95% alcohol, is used. The urine is rendered distinctly acid to turmeric by means of acetic acid, and filtered, and 50 c.c. of the filtrate heated to incipient boiling, left for a few minutes, and then treated with 5 c.c. of the reagent and the flask shaken with a rotatory movement. As soon as the precipitate is coagulated, the liquid is filtered through counterpoised filter papers, and the precipitate washed first with boiling water and finally with a mixture of alcohol and ether, and dried at 100° until constant in weight.

C. A. M.

Action of Hydrogen Peroxide on Flours. MARION (*Compt. rend.*, 1920, **171**, 804—806).—The amount of catalase differs from one sample of flour to another. It is most prevalent in milling offals and least in high-grade flour. Measurement of the amount of decomposition of a definite volume of hydrogen peroxide by a given weight of flour in a given time gives a means of determining the percentage of extraction of the flour.

W. G.

The Indices of Enzymes of the Blood. Estimation of the Catalase, Peroxydase and, Esterase in a Drop of Blood. A. BACH and (MME) SOPHIE ZOUBKOFF (*Compt. rend.*, 1920, **171**, 967—969).—For the test, 0·02 c.c. of the blood is diluted with 10 c.c. of water, and 1 c.c. of this solution is used for each test. The catalase activity is measured by the amount of hydrogen peroxide decomposed under given conditions and the peroxydase activity by the amount of guaiacol oxidised in the presence of hydrogen peroxide as compared with the effect from 1 c.c. of the diluted blood, previously boiled. This estimation is colorimetric. For the measurement of the esterase activity, advantage is taken of the fact that phenolic esters are not oxidised by the system peroxydase-hydrogen peroxide, whereas free phenols are readily oxidised.

W. G.

Biological Methods for the Estimation of Substances which Injure the Cell and its Reproducing Capacity. I. Optochin. ALFRED SCHNABEL (*Biochem. Zeitsch.*, 1920, **108**, 258—279).—Dilutions of optochin of one in several millions can be estimated by utilising its action on the reduction of methylene-blue by *Pneumococci*. The greatest dilutions can be estimated at the ordinary temperature, but more exact results are obtained at a temperature of 37°. The concentrations of optochin solutions which can be estimated are also influenced by the number of bacteria and the duration of action. S. S. Z.

Measurement of the Lachrymatory Power of Irritant Substances by the "Sill" Method. CHARLES DUFRAISSE and JACQUES CH. BONGRAND (*Compt. rend.*, 1920, **171**, 817—819).—The method consists in determining the concentration of the substance required in an atmosphere just to produce the first irritant sensation on the eyes at the end of thirty seconds' exposure. Benzyl bromide was taken as the standard. By this method, the lachrymatory power was independent of the observer, although the actual concentration for the gases might vary in the same proportion from one observer to another. W. G.

The Properties of Lachrymatory Substances and the Measure of their Activity. GABRIEL BERTRAND (*Compt. rend.*, 1920, **171**, 965—967).—It is shown that the minimum concentration of a lachrymatory substance which is perceptible depends, not only on the observer, but on the duration of the exposnre. With some substances the effect is immediate, and increases but little in intensity with time, whilst with others there is marked increase in intensity with the time. In consequence, the method of Dufraisse and Bongrand (preceding abstract) does not give a correct comparison between different lachrymatory substances. W. G.

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